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Partitioning and Reversibility of Polymer Adsorption in the Polystyrene, 1,2-Dichloroethane, Carbon Black System

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PARTITIONING AND REVERSIBILITY OF POLYMER ADSORPTION IN THE POLYSTYRENE, 1,2-DICHLOROETHANE, CARBON BLACK SYSTEM

A thesis submitted by

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SUMMARY

In the theoretical studies of a polymer adsorption system at equilibrium, it is generally assumed that the system has attained thermodynamic equilibrium. The object of this investigation was to study the validity of this assumption.

A system of polystyrene, 1,2-dichloroethane, and a graphitized carbon black as the adsorbate, solvent, and adsorbent, respectively, was selected. Polystyrene samples of broad and narrow molecular weight distributions were employed. The graphitized carbon black was nonporous. This system is believed to involve only adsorption forces of the van der Waals' type, i.e., physical adsorption.

Polystyrene solutions were mixed with carbon black samples for specified times, four days were allowed for equilibration, the supernatant solutions were separated, and the isolated solutions were analyzed for intrinsic viscosity and concentration. The amount of polymer adsorbed was calculated from measurements of the solution concentration before and after adsorption. The intrinsic viscosity determinations were used as a measure of the average molecular weight of the polymer solutions.

Sedimentation coefficient distributions were obtained for selected supernatant solutions. These distributions were determined from sedimentation-velocity experiments on an ultracentrifuge and were corrected for the effects of pressure, diffusion, and concentration.

The reversibility of polymer adsorption with respect to the molecular weight of the polymer was investigated by varying the order of addition of polymers having varying molecular weights to the adsorption system. It was found that the average molecular weight of the adsorbed polymers at equilibrium was independent of their order of addition.

Broad molecular weight distribution polymer samples were found to be fractionated by preferential adsorption of the high molecular weight species. The average molecular weight of the adsorbed polymer was found to be dependent only on the weight fraction of polymer adsorbed.

The adsorption isotherms were found to be of the Langmuir type over the range of concentrations studied. At equivalent concentrations, a high molecular weight sample was found to have a greater specific adsorption than a lower molecular weight sample.

The sedimentation coefficient distributions of several polymer samples before and after adsorption were determined. A partitioning expression was derived from these data such that for any degree of polymerization, D.P., a ratio between the number of molecules of this D.P. in the adsorbed and supernatant phases was related to the D.P. of the molecule. This expression was found to have nearly the same functional form as a theoretical expression derived from statistical thermodynamics.

The reversibility results together with the developed partitioning expression provide good evidence that the adsorption system attained thermodynamic equilibrium.

INTRODUCTION

The importance of polymer adsorption extends from biological to industrial applications. The systematic analysis of the adsorption of polymer molecules is more difficult than that for the adsorption of low molecular weight adsorbates. One of the obvious differences between polymer adsorption and, for example, gas adsorption is the size, i.e., molecular weight, of the adsorbate. The effect of polymolecularity upon a polymer adsorption system was the purpose of this study.

Several papers have been published on the theoretical analysis of polymer adsorption (1-8). To facilitate the application of thermodynamics to the analysis, these papers have assumed that a polymer adsorption system attains thermodynamic equilibrium. Analysis of the thermodynamic state functions of the system could be used to demonstrate thermodynamic equilibrium; however, an analysis of this type in a liquid solution is difficult and the characteristics of a polymer solution increase the complexity of this type of analysis.

Although the demonstration of reversibility in a system is not sufficient to prove thermodynamic equilibrium, it is a condition of thermodynamic equilibrium and should provide good evidence for it. One of the objectives of this work was to study the equilibrium condition of a polymer adsorption system to determine the reversibility of the system with respect to molecular weight. Studies of the reversibility of polymer adsorption systems have been made by several techniques for some of the system variables.

LITERATURE REVIEW

REVERSIBILITY WITH RESPECT TO CONCENTRATION

The most common of the reversibility experiments has been the replacement, after equilibrium was established, of the bulk phase with pure solvent. (The term bulk phase is used throughout this thesis to indicate the solution phase.) Most of the literature on the desorption of polymers with solvent indicates that desorption does not occur or that only a small fraction of the adsorbed polymer is desorbed (9-19). Gilliland and Gutoff (10) reported that nearly all of the low molecular weight polyisobutylene was desorbed from carbon black after extraction with solvent for one month. The higher molecular weight polyisobutylene, however, was not desorbed to the same extent. Stromberg, et al. (19) studied the adsorption and desorption of C^{14}-tagged polystyrene and found the desorption dependent on the amount of polymer adsorbed. It was found that the path to attaining a given amount of adsorbed polymer did not affect the rate of desorption of the polymer, and the rate of desorption increased with increased amounts of adsorbed polymer. However, it was not possible in any instance to remove all of the polymer from the surface phase with desorption periods up to three weeks.

Stromberg, et al. (19) explained their desorption results on the basis that fewer segments of a polymer molecule were adsorbed at high adsorption levels than at low adsorption levels. Since each adsorbed segment of the polymer must desorb before the molecule can diffuse away from the surface, it is to be expected that high adsorption levels would result in a higher rate of desorption than would lower levels. Stromberg's data were obtained by radiochemically analyzing the adsorbed polymer, rather than the more conventional methods of analyzing the bulk phase. It is possible that desorption in other systems does occur as Stromberg found, but the techniques used in analyzing the bulk phase may not have been sensitive enough to detect the small amount of polymer desorbed.

Silberberg (2) has considered this problem of apparent irreversibility of polymer adsorption and concluded that the polymer is not desorbed because the surface remains in equilibrium with the solvent. In other words, the adsorbed polymer has created an environment at the surface such that even large changes in the bulk phase have little effect on the polymer adsorption sites because the concentration of polymer near the surface is not changed.

REVERSIBILITY WITH RESPECT TO TEMPERATURE

The theoretical discussions on polymer adsorption indicate that the temperature coefficient may be either positive or negative depending on the system studied, but the coefficient is predicted to be small in either case (1-4). This has been established experimentally (14,17,20,21). Although the change in adsorption with temperature is small, differences in adsorption can be measured over a 30 to 50°C. temperature change. The change of adsorption with temperature has been used to study the reversibility of polymer adsorption. In general, the techniques consist of equilibration of the adsorption system at one temperature followed by reequilibration at another temperature. The results of these investigations depend on the system studied.

Stromberg and Kline (17) studied the adsorption of polyneopentylsuccinate on glass and found that the polymer could be desorbed from the glass by increasing the temperature from 30 to 87°C. A later study by Stromberg and Grant (21) with polyethylene o-phthalate demonstrated that the adsorption was greater at 50°C. than at 0°C. Desorption of polymer, to an equivalent level attained by isothermal adsorption at 50°C., was observed from a sample equilibrated at 0°C. and then re-equilibrated at 50°C., but adsorption did not occur by cooling an equilibrated sample from 50 to 0°C. However, if the adsorbent, glass, was exposed to water vapor, reversibility in both directions was observed. Stromberg suggested that

the adsorbed water vapor caused weaker interactions between the adsorbent and polymer. Ellerstein, et al. (20) studied the reversibility with respect to temperature of polymethylmethacrylate on iron powder. It was found that the polymer could be desorbed by increasing the temperature, but readsorption of polymer did not occur by decreasing the temperature of the system.

On the basis of Stromberg and Grant's results (21), the reversibility with respect to temperature is dependent on the strength of the polymer-adsorbent interaction. When the polymer is strongly adsorbed, complete reversibility is not obtained, at least within the 1-2 days allowed for equilibration, but with weaker adsorption forces reversibility is observed.

REVERSIBILITY WITH RESPECT TO SOLVENTS

A unique experiment by Ellerstein, et al. (20) with an acetonitrile-benzene solvent mixture demonstrated the reversibility of polymer adsorption with respect to solvent. Two solutions of polymethylmethacrylate were prepared; one with 100% benzene, and the other with 75% benzene and 25% acetonitrile. Equal amounts of adsorbent were added to each solution and equilibrium was established. Both systems were then adjusted to 80% benzene and 20% acetonitrile by appropriate addition of the respective solvents and the systems were reequilibrated. It was found that both systems attained the same equilibrium condition by either path.

REVERSIBILITY WITH RESPECT TO MOLECULAR WEIGHT

Kolthoff and Gutmacher (9) studied the reversibility of polymer adsorption with respect to molecular weight. In these experiments, a high molecular weight rubber was found to displace a portion of previously adsorbed low molecular weight rubber and the lows would also replace some of the previously adsorbed highs. A similar set of experiments reported by Emery (22) gave equivalent results using

narrow molecular weight distribution polystyrene. These experiments indicate that polymer adsorption is reversible with respect to molecular weight, but there have been no quantitative measures of this phenomenon.

The experiments cited above on the reversibility of polymer adsorption indicate that adsorption is reversible under certain conditions. The experiments by Stromberg, et al. (19), on the desorption of polymer with pure solvent, show partial reversibility. Other experiments by Stromberg, et al. (17,21) and Ellerstein, et al. (20) show both complete and partial reversibility with respect to temperature. It was hypothesized by Ellerstein and Stromberg that the system was reversible with respect to temperature in both adsorption and desorption, but the adsorption of polymer was too slow to be detected. Ellerstein, et al. (20) demonstrated that the adsorption was reversible with mixed solvents, but this phenomenon was not extensively studied. The work of Kolthoff and Gutmacher (9) and Emery (22) indicate that the adsorption is reversible with respect to molecular weight, but these experiments were qualitative in nature.

The quantitative demonstration of reversibility with respect to molecular weight, together with the evidence for reversibility in the literature, would be good evidence that this requirement of thermodynamic equilibrium was satisfied. For a system at thermodynamic equilibrium, a definable relationship between the polymer homologues in the surface and bulk phases should exist. Some experimental and theoretical investigations have been made to determine such a relationship.

PARTITIONING OF POLYMER HOMOLOGUES

Emery (22) described the adsorption equilibrium of polystyrene from 1,2-dichloroethane by measuring the intrinsic viscosity of the bulk phase as a function of the weight fraction of polymers adsorbed. From an analysis of the molecular

weight distribution of the polymer before and after adsorption, Emery also found that the partitioning of a polymeric species between the bulk and surface phases could be expressed as a function of its degree of polymerization. This expression, however, was not in agreement with a theoretical expression developed by Gilliland and Gutoff (4). Emery concluded that this lack of agreement resulted from the oversimplified model used by Gilliland and Gutoff.

Several other theoretical papers which are concerned with the description of a polymer at a liquid-solid interface, i.e., Simha, Frisch, and Eirich (SFE) (1), Silberberg (2), and Forsman and Hughes (3), do not readily lend themselves to a description of the partitioning of a polymer homologue between the surface and bulk phases. The dissertations by SFE and Forsman and Hughes are based on reflecting statistics which have been criticized by Silberberg (2) and DiMarzio (8). The treatment by Silberberg (2) has recently received criticism by Hoeve, DiMarzio, and Peyser (5), DiMarzio (8), and Roe (6) to the effect that Silberberg used an incorrect combinational factor in deriving his partition expression for a single polymer molecule at an interface.

Hoeve, DiMarzio, and Peyser (5), on the basis of statistical thermodynamics, derived an expression for the conformation of an isolated polymer at a solid-liquid interface. Their results were in agreement with those found by Roe (6), who evaluated the same problem from a slightly different approach. Hoeve, DiMarzio, and Peyser extended their results to describe the partitioning of a polymer homologue between the bulk and surface phases at low levels of adsorption. The limitations in their derivation were that the polymers be large enough that end effects could be neglected, and that the polymer-solvent interactions be of the same order as the polymer-polymer interactions, i.e., the adsorption takes place from a theta solvent. In a later paper, Hoeve (7) considered the partitioning

problem at higher levels of adsorption by allowing polymer-polymer interactions in the surface phase, and found the partitioning expression to have the same form as before. This partitioning expression is given by Equation (1):

$$N_p/A\delta = (N_f/V) \exp(-\lambda n) \qquad (1)$$

where the terms are defined as follows:

$\underline{n}$ = number of segments per polymer, related to the degree of polymerization (D.P.)

$\underline{N_p}$ = number of polymers containing $\underline{n}$ segments in the surface phase

$\underline{N_f}$ = number of polymers containing $\underline{n}$ segments in the bulk phase

$\underline{A}$ = surface area of adsorbent

$\underline{V}$ = volume of solution

λ = Lagrangian multiplier, a measure of the conformation of an adsorbed polymer

δ = a characteristic surface to adsorbed segment distance

This treatment assumes, of course, that equilibrium thermodynamics can be applied to polymer adsorption.

SCOPE AND APPROACH

The purpose of the present study was to investigate the equilibrium state of a polymer adsorption system with the objectives of defining a partitioning expression and of demonstrating reversibility with respect to molecular weight for the system. The demonstration of reversibility would be evidence for thermodynamic equilibrium, and would indicate that a derived partitioning expression was representative of a system at equilibrium. The definition of such an expression would be of importance to further studies of polymer adsorption.

A system of polystyrene, 1,2-dichloroethane, and graphitized carbon black was selected. Emery (22) has demonstrated that the characteristics of this system were satisfactory to study the molecular weight effects of a polymer adsorption system. Some of the advantages of this system were that it had been studied previously. Polystyrene is a well-known polymer and its hydrodynamic behavior has been studied extensively in a variety of solvents. 1,2-Dichloroethane is readily purified, and the graphitized carbon black was nonporous. It can be seen from the components of the system that there should be no strong chemical interactions or hydrogen bonding between the components. This suggests that the adsorption forces would be physical in nature, i.e., of the van der Waals' type.

The reversibility experiments were similar to those used by Emery (22) and Kolthoff and Gutmacher (9), but the experiments were modified slightly to provide quantitative information about the equilibrium condition. The development of a partitioning expression involved the determination of the molecular weight distribution of polymer samples at several selected equilibrium conditions.

EXPERIMENTAL EQUIPMENT, MATERIALS, AND PROCEDURES

DESCRIPTION, PURIFICATION, AND CHARACTERIZATION OF MATERIALS

POLYSTYRENE

Samples

Broad distribution samples of Polystyrene were provided by Dr. H. W. McCormick of the Dow Chemical Company, Midland, Michigan. Two of these samples, Polystyrene B5 and B6, were used in this study.

Samples of narrow molecular weight distribution, Polystyrene S103 and S108, were kindly provided by Dr. J. F. Rudd of the Dow Chemical Company, Midland, Michigan, and Sample L10 by Mr. T. Altares, Jr., of the Mellon Institute, Pittsburgh, Pennsylvania.

Purification

The polystyrene samples were purified by dropwise precipitation from a solution of benzene into two volumes of ice-cold methanol. After decanting the supernatant, the polymer was redissolved in benzene and the procedure was repeated three times. The details of the method have been given by Emery (22). The final precipitate was dissolved in distilled benzene, concentrated to approximately 10% and freeze-dried on an N.R.C. type 3505-2 dehydration unit (NRC Equipment Corporation, Newton Highlands, Massachusetts). The resultant dry polymer was fluffy and redissolved readily.

Characterization

Intrinsic viscosities of the purified polymers $[\eta]_o$, were determined in 1,2-dichloroethane at 30.0°C., and the weight- and number-average molecular weights of the broad distribution samples were calculated from the distributions obtained by

sedimentation velocity ultracentrifuge analysis at 35°C. in cyclohexane. These results are presented in Table I. Complementary information regarding physical characterization of the Dow samples has been reported (22-26).

TABLE I

CHARACTERIZATION OF POLYSTYRENE SAMPLES

Sample	$[\eta]_o$, dl./g.	$\overline{M}_w \times 10^{-5}$	$\overline{M}_w/\overline{M}_n$
PB6[a]	1.104	4.39	2.46
PB5[a]	0.782	2.98	1.97
PS103[b]	0.469	1.24[c]	1.05[c]
PS108[b]	0.771	2.67[c]	1.08[c]
PL10[b]	1.486	6.25[c]	--

[a] Prepared by isothermal polymerization; yields a broad molecular weight distribution of polymers.

[b] Prepared by anionic polymerization; yields a narrow molecular weight distribution of polymers.

[c] Values reported for original samples.

1,2-DICHLOROETHANE

Purification

The procedure used to purify 1,2-dichloroethane has been reported by Emery (22) as a modification of that employed by Barton and Howlett (27). Reagent-grade solvent (Matheson, Coleman, and Bell Company, b.p. 84-85°C.) was shaken thoroughly with concentrated sulfuric acid, followed by successive washings with 1N sodium hydroxide, a saturated aqueous solution of sodium bicarbonate, and distilled water. The washed solvent was dried over calcium chloride and then twice fractionally distilled from reagent-grade phosphorus pentoxide in an atmosphere of

dry nitrogen. The distillations were carried out in a 3-ft. column packed with 6 by 6-mm. glass Raschig rings.

Solvent Quality

As suggested by Maclean, et al. (28), the solvent quality was determined by ultraviolet spectrometry. The purity of the solvent was increased substantially over the reagent grade by the purification process. This degree of purity, equivalent to that of spectrograde solvent (Matheson, Coleman, and Bell), was reproducibly attained with the purification process. Typical absorbance values are presented in Table II.

TABLE II

ULTRAVIOLET ABSORBANCE OF 1,2-DICHLOROETHANE SAMPLES AGAINST DISTILLED WATER

Wavelength, nm.	Absorbance		
	Reagent	Spectroquality	Purified
225	--	1.03	1.03
226	--	0.812	0.809
228	1.53	0.531	0.559
230	1.17	0.343	0.374
235	0.621	0.123	0.140
240	0.322	0.052	0.056
245	0.157	0.026	0.022
250	0.076	0.013	0.008
255	0.043	0.008	0.003
260	0.029	0.002	0.001

The density of a sample of purified solvent, as determined with a Sprengle pycnometer at 30.0°C., was found to be 1.23851 g./ml. This value was in good agreement with values of 1.23903 and 1.23831 g./ml. reported by Emery (22) and Timmermans and Martin (29), respectively.

CYCLOHEXANE

Reagent-grade cyclohexane (Matheson, Coleman, and Bell Company, m.p. 5-6°C.) was treated with an acidic solution of potassium permanganate and passed through a column of activated silica gel as described by Trice (30). Prior to use, the purified solvent was distilled and the middle 40% of the distillate was used.

GRAPHITIZED CARBON BLACK

Samples

Graphitized carbon black, known as Sterling FT-D4, was obtained from Cabot Corporation, Boston, Massachusetts. Considerable evidence (31-39) has established that graphitized carbon blacks consist of nonporous particles with uniform surface characteristics.

Purification

This graphitized carbon black sample was shown by Emery (22) to contain contaminants which increased the ultraviolet absorbance values of the solvent during short exposure times to the carbon black. Emery (22) found that these contaminants could be removed by heating the graphitized carbon black to 600°C. for 24 hours. A similar treatment was used in this work, except the heating was done *in vacuo* to prevent oxidation of the samples.

To determine the effectiveness of the treatment, samples of treated and untreated carbon black were mixed with solvent and agitated for 24 hours. The solvent was then decanted, filtered through a type AA (0.8 μm.) Millipore filter, and analyzed for its ultraviolet absorbance values. The results of the experiments are shown in Table III. Apparently, the furnace treatment removed the contaminating materials; therefore, this treatment, 24 hr. at 600°C. *in vacuo*, was employed to purify the adsorbent.

TABLE III

ULTRAVIOLET ABSORBANCE OF SOLVENT BEFORE AND AFTER EXPOSURE TO GRAPHITIZED CARBON BLACK

Wavelength, nm.	Ultraviolet Absorbance[a]		
	A	B	C
225	1.03	1.14	1.06
226	0.825	0.93	0.855
228	0.543	0.625	0.559
230	0.350	0.426	0.359
235	0.107	0.171	0.111
240	0.023	0.082	0.026
245	0.000	0.048	0.000
250	0.000	0.036	0.000

[a]Code: A - control solvent; B - 15 ml. of solvent exposed to 2 g. of untreated carbon black; C - 15 ml. of solvent exposed to 2 g. of furnace-treated carbon black.

Upon removal from the furnace, the adsorbent was placed in a vacuum desiccator (over P_2O_5 which was immediately evacuated and refilled with prepurified nitrogen. Adsorbents were stored in this manner until used.

Characterization

No characterization of the adsorbent was made in this study, but Emery (22) determined the surface area of the untreated adsorbent to be 11.91 $m.^2/g.$ as measured by nitrogen gas adsorption. Electron micrographs by the same author showed the carbon black particles to be regular polyhedra. This was in agreement with other work (31,32,40,41).

DETERMINATION OF SOLUTION CONCENTRATIONS

GRAVIMETRIC METHOD

Solution concentrations used in this study were determined gravimetrically. To evaluate the drying procedure used in the gravimetric concentration determination, a quantitative solution of Polystyrene PB6 was prepared (0.56550%). Two 10-ml. samples of the solution were weighed and the solvent evaporated. The weight of the residue was then determined (with an Ainsworth semimicro balance) for successive periods of drying in vacuo at 106°C. The data are presented in Table IV.

TABLE IV

EVALUATION OF DRYING PROCEDURE FOR CONCENTRATION DETERMINATIONS BY GRAVIMETRIC ANALYSIS[a]

Total Drying Time[b], hr.	Apparent Concentration	
	Sample 1	Sample 2
18	0.56599	0.56553
40	0.56546	0.56519
56	0.56533	0.56535
84	0.56554	0.56547
96	0.56565	0.56562

[a] Concentration of starting solution: 0.56550% by weight Polystyrene PB6 in 1,2-dichloroethane.

[b] Drying time in vacuo at 106°C.

For drying times between 40 and 96 hr., the deviations between the actual and apparent concentrations did not exceed 0.06%. These results are in agreement with those found by Emery (22) for the same system. Drying times between 75 and 100 hr. in vacuo at 106°C. were used for the gravimetric concentration determination.

CONVERSION OF GRAVIMETRIC CONCENTRATION TO VOLUMETRIC CONCENTRATION

Because of the need for volumetric concentrations in viscometry, the gravimetric concentrations were converted to volumetric quantities with consideration of the partial specific volume of the polymer in solution, $\emptyset$, as shown in Equation (2).

$$C_V = \rho C_W = C_W \rho_o / [1 + (\emptyset \rho_o - 1) C_W / 100] \qquad (2)$$

where ρ_o and ρ are the solvent and solution densities, respectively, and $\underline{C_V}$ and $\underline{C_W}$ are the volumetric and gravimetric concentrations, respectively, expressed as percents. Since the concentrations employed in this study were dilute, $\underline{C_W}$ less than 0.6%, the partial specific volume was assumed to be independent of concentration.

To determine the partial specific volume of polystyrene in 1,2-dichloroethane, solution ($\underline{C_W}$ = 0.5655%) and solvent densities were determined at 30.0°C., yielding respective values of 1.23740 g./ml. and 1.23851 g./ml. Utilizing these quantities in Equation (2), a value of 0.93 ml./g. was obtained for $\emptyset$. This compared well with the value of 0.89 ml./g. determined by Emery (22) for polystyrene in 1,2-dichloroethane at 30.0°C.

INTRINSIC VISCOSITY DETERMINATIONS

EXTRAPOLATIVE METHOD

Solvent and solution viscosities were determined at 30.0 ± 0.01°C. in 1,2-dichloroethane with Cannon Ubbelohde semimicro viscometers (size 25) having solvent efflux times of 255 and 160 sec. Since it has been demonstrated that the kinetic energy correction (43) and the effect of rate of shear (44,45) are

negligible under the conditions employed, the solution viscosities were directly proportional to the observed efflux times. In this case, the specific viscosity, η_{sp}, and the relative viscosity, η_r, are defined by Equations (3) and (4).

$$\eta_{sp} = (t_s - t_o)/t_o \tag{3}$$

$$\eta_r = t_s/t_o \tag{4}$$

where t_s and t_o are the respective solution and solvent efflux times.

Cleanliness was found to be very important when measuring the solution and solvent efflux times; therefore, each solution was filtered repeatedly through a type AA (0.8 μm.) Millipore filter and then directly into the viscometer. Efflux times were recorded to the nearest tenth of a second, and a minimum of five readings were taken. In all cases, dilution techniques were avoided; each solution was prepared on a weight basis.

The intrinsic viscosity, $[\eta]_o$, and the constants, k_α and k_β, were determined from measurements of η_{sp} and η_r at several volumetric solution concentrations according to the following mutually related equations (46,47):

$$\eta_{sp}/C_v = [\eta]_o + k_\alpha [\eta]_o^2 C_v \tag{5}$$

$$[\ln(\eta_r)]/C_v = [\eta]_o - k_\beta [\eta]_o^2 C_v \tag{6}.$$

These data are shown in Fig. 1.

The constants, k_α and k_β, are characteristic of a given solvent-polymer pair and temperature, independent of molecular weight, and related as follows:

$$k_\alpha + k_\beta = 0.5 \tag{7}.$$

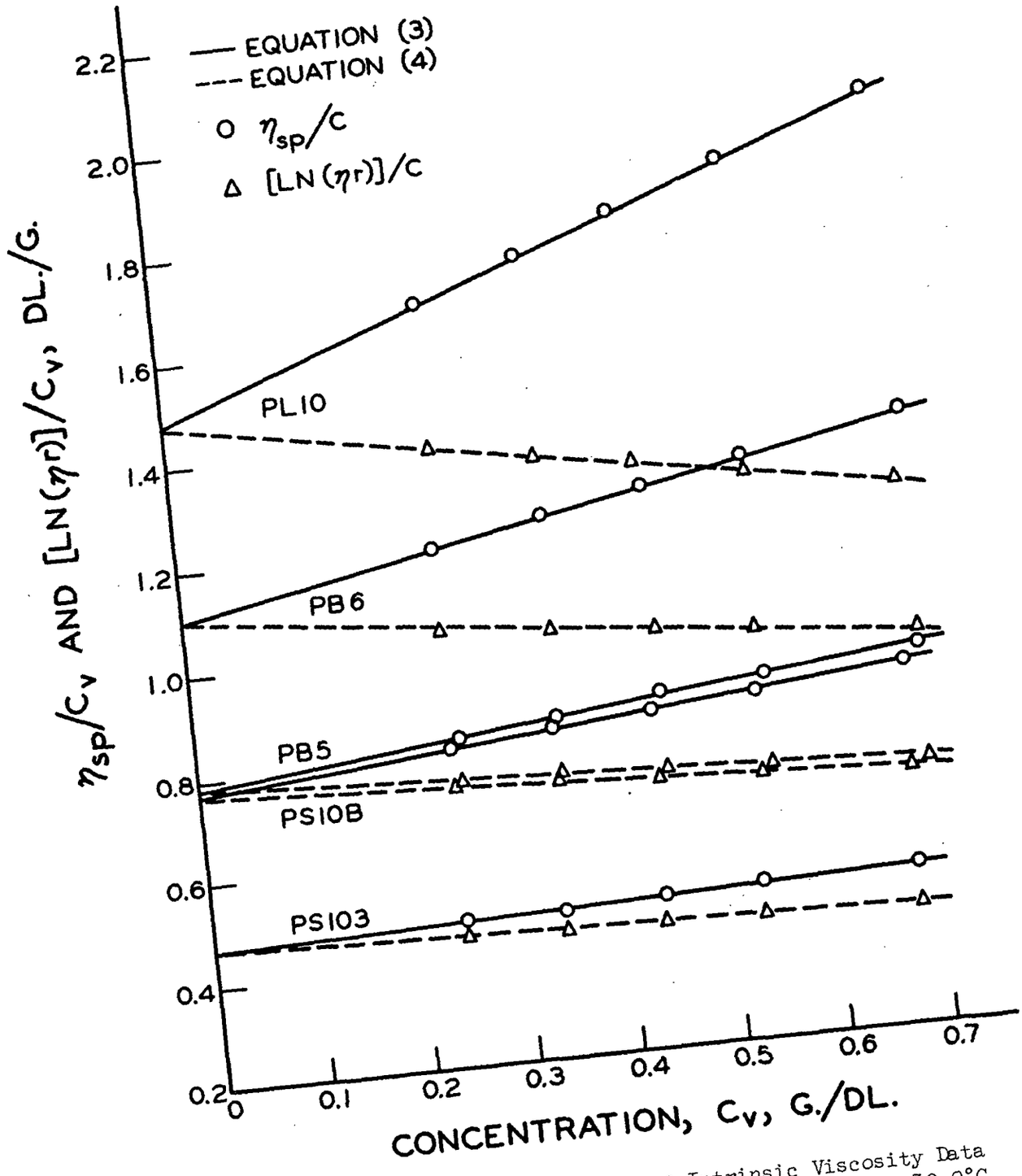

Figure 1. Concentration Extrapolation of Intrinsic Viscosity Data for Polystyrene Samples in 1,2-Dichloroethane at 30.0°C.

The extrapolated values of the intrinsic viscosity are tabulated in Table V with the appropriate constants for each polymer sample.

TABLE V

SUMMARY OF INTRINSIC VISCOSITY RESULTS

Polystyrene Sample	$[\eta]_o$, dl./g.	k_α	k_α/k_β	$k_\alpha + k_\beta$
PB6	1.104	0.325	2.07	0.481
PB5	0.782	0.363	2.55	0.506
PS103	0.469	0.327	1.94	0.495
PL10	1.486	0.332	2.26	0.480
PS108	0.771	0.331	2.05	0.491

ONE-POINT METHOD

Because of the time and quantity of solution required by the above method of determining intrinsic viscosities, a one-point method was used for the adsorption experiments. Maron (48) has combined Equations (5) and (6) to develop the working equation for the one-point method.

$$[\eta] = \left\{\eta_{sp} + \gamma[\ln(\eta_r)]\right\}/[(1 + \gamma)C_v] \qquad (8)$$

where

$$\gamma = k_\alpha/k_\beta \qquad (9)$$

The constant, γ, is tabulated in Table V for each polymer sample.

ADSORPTION RUNS

CLEANING PROCEDURES

To minimize the chance of impurities being introduced in the adsorption system, considerable care was taken to clean the equipment. All glassware was cleaned by

the following procedure: a thorough washing with detergent, sequential heating to near boiling in toluene and alcoholic-KOH, steeping overnight in a 6% hydrogen peroxide-6N hydrochloric acid solution, and a thorough rinsing in distilled water. The glassware was then dried at 115°C. in a clean oven and stored in a desiccator. The Teflon seals for the adsorption tubes were cleaned by the same procedure and the drying was done at 40°C. in vacuo.

APPARATUS

The adsorption experiments were carried out in 50-ml. centrifuge tubes fitted with screw caps which had an inner cushion of rubber and a Teflon liner.

The tubes were agitated during an adsorption run at 25°C. in a temperature-controlled water bath. The agitation was provided by mounting the tubes on the periphery of a 12-inch diameter wheel at a fixed angle of 15° to the wheel's centrally mounted shaft. The shaft and attached wheel were rotated at a speed of 30 r.p.m.

PROCEDURE

Preliminary Preparation

Enough solvent and carbon black were purified prior to the start of a series of experiments to insure a constant quality of components. A portion of the purified polymer was used to make a stock solution and the concentration was determined gravimetrically. Solutions of lower concentration were prepared on a weight basis from a stock solution.

The required 0.5 to 5.0 g. of purified carbon black were weighed by difference into the adsorption tubes to $\pm$ 0.3 mg. The tubes and black were heated at 115°C. for at least 12 hr. and then cooled in a vacuum desiccator filled with prepurified nitrogen.

Initiation of the Adsorption Run

The adsorption run was initiated by addition of the polymer solution (at 25.0°C.) from volumetric pipets into the tubes containing the carbon black. The tubes were sealed by stretching Teflon film across the mouth of each tube and securing the screw caps. The caps were sealed to the tubes with waterproof tape and mounted on the rotator in the water bath.

Equilibration Period

Emery (22) has shown previously that at least three days are required to attain equilibrium with this adsorption system. To confirm that equilibrium had been established, a series of adsorption runs were made with equilibration times between four and fifteen days. Both the intrinsic viscosity of the bulk phase, $[\eta]_B$, and the specific adsorption, Γ, were measured as a function of time. The results of these experiments are presented in Table VI and demonstrate that there is no significant change in the equilibrium condition between 4 and 15 days. The significance level chosen was the 95% confidence level as determined from the fractionation data presented in the Discussion section.

TABLE VI

ADSORPTION OF POLYSTYRENE PB6 AS A FUNCTION OF TIME

Contact Time, days	$[\eta]_B$, dl./g.	Γ, mg./g.
4	0.695	15.4
5	0.697	15.0
7	0.698	15.0
15	0.679	14.8

These results, together with those obtained by Emery, are good evidence that polymer degradation does not occur to an appreciable extent in this system. Emery

found that the intrinsic viscosity of the bulk phase decreased to a minimum value in 3 days and remained unchanged for an additional day. This study shows that the intrinsic viscosity is constant between 4 and 15 days.

Separation of Adsorbent and Solution

After the desired contact time, the solution and adsorbent were separated by centrifugation of the intact adsorption tubes for 30 minutes under a force of approximately 3000 g. The supernatant was decanted to a clean centrifuge tube, and centrifuged as before. The supernatant was again decanted and filtered at least three times through a type AA (0.8 μm.) Millipore filter to remove any suspended carbon black.

To determine the efficiency of the filtration, furnace-treated carbon black was mixed with the solvent and filtered as above. No residue of carbon black was detected after evaporation of the filtered solvent. Also, no carbon black was observed in any of the polymer residues used for the gravimetric determinations of the solution concentration.

It was also determined that the filtration steps did not remove polymer from solution. This was studied by measuring the efflux times of a polymer solution before and after filtration. No change in the efflux time could be detected.

Analysis

In each adsorption experiment, the efflux time and the gravimetric concentration were determined on the isolated bulk phase. From these measurements, the amount of polymer adsorbed and the intrinsic viscosity of the bulk phase were calculated.

When it was desired to determine the molecular weight distribution of the polymer from the bulk phase of an adsorption experiment, a portion of the sample was retained to be analyzed with the ultracentrifuge.

DETERMINATION OF SEDIMENTATION COEFFICIENT DISTRIBUTIONS FROM SEDIMENTATION VELOCITY EXPERIMENTS WITH AN ULTRACENTRIFUGE

INTRODUCTION

Ultracentrifuge analyses were made to determine the sedimentation coefficient distribution of selected polymer samples. The mathematical theory of ultracentrifugation and its application to determination of the distribution of sedimentation coefficients has been presented by Fujita (49). For the particular procedures used for the analysis of this work, the study by Emery (22) was of major assistance.

In the sedimentation velocity method, the transport of an initially sharp boundary between the solution and solvent is followed as a function of time. Spreading of the boundary, under the appropriate conditions, results primarily from polymolecularity effects. Other effects which influence the spreading of the boundary, such as concentration, diffusion, and pressure, are corrected for in the boundary spreading analysis. The result of these calculations is the distribution of the sedimentation coefficients of the polymer sample analyzed. The calculation of molecular weight distribution requires further experiments to determine the relationship between sedimentation coefficient and molecular weight.

EXPERIMENTAL

Choice of Solvent

To minimize concentration corrections, a theta solvent was used in the ultracentrifuge analyses. The theta temperature for a polystyrene – cyclohexane system has been found (50,51) to be in the temperature range of 34.0 to 34.5°C. To prevent possible phase separation, the ultracentrifuge work was done at 35.0°C.

Preparation of Samples

The samples from the adsorption experiments to be analyzed on the ultracentrifuge were placed in solvent-extracted aluminum weighing dishes, evaporated at 40°C., and then dried *in vacuo* at 60°C. for at least 48 hr. The aluminum weighing dishes with their dried polystyrene films were then cut into strips and placed in volumetric flasks. Care was taken to transfer all of the film into the flask to avoid possible fractionation of the sample. When a sample was to be analyzed, purified cyclohexane was added and the sample was placed in a 37°C. oven for a day.

To prevent possible phase separation in the solution-transfer steps, all cell components, syringes and solutions were warmed to 50°C. before the cell was filled.

Equipment and Procedures

The sedimentation velocity experiments were made on a Spinco Model E Analytical Ultracentrifuge which was equipped with a RTIC (temperature controlling) unit and a high temperature heater. The optics of the instrument were aligned using the procedure described by Gropper (52). A single sector synthetic boundary centerpiece and sapphire windows were assembled in a cell housing and mounted in an ordinary An-D analytical rotor.

Before mounting the prewarmed loaded cell into the rotor, the rotor was warmed to 35°C. The cell and counterbalance were then aligned in the rotor and the assembly mounted in the ultracentrifuge. After evacuation of the rotor chamber, the rotor was equilibrated at 35°C. for at least one-half hour before the run was initiated.

During acceleration, the high temperature unit and the refrigeration were used to minimize temperature gradients in the cell which resulted from the

adiabetic cooling of the rotor. At speed, 56,100 r.p.m., only the RTIC unit was used for temperature control. During acceleration, speed-time data were recorded to facilitate calculation of the equivalent time at 56,100 r.p.m. Schlieren photographs were taken at two-minute intervals after the initiation of the run.

Schlieren photographs were analyzed with a modified Wilder microcomparator which provided a magnification factor of 40X. The X-Y stage on the comparator was fitted with micrometers that were read to the nearest 0.0001 inch.

CALCULATION OF SEDIMENTATION COEFFICIENT DISTRIBUTION

Calculation of Apparent Distribution

The boundary, as measured from the schlieren photographs, may be converted to the distribution of sedimentation coefficients as presented below, but this distribution must be corrected for the effects of pressure, diffusion, and concentration.

To account for the transport of the boundary during acceleration, the time required for acceleration is converted to an equivalent time, t_e, at maximum speed, ω_f. This calculation is made by recording the speed-time, ω-t, data during acceleration and numerically integrating according to Equation (10).

$$t_e = (1/\omega_f^2) \int_o^t \omega^2 \, dt \tag{10}$$

The sedimentation coefficient, S, at any point on the boundary is readily defined by (52)

$$S_i^* = (1/\omega_f^2 t_e) \ln (r_i/r_o) \tag{11}$$

where r_i and r_o are defined as the distances from the center of rotation to the ith species in the boundary and the original boundary, respectively. The extrapolation

procedure for computing the original boundary location from early photographs has been described by Emery (22). The apparent differential weight distribution function, $g^*(S)$, is given by (49):

$$g^*(S_i) = \omega_f^2 t_e \, r_i 3(\partial\overline{\Delta n}/\partial r)_i / \int_o^\infty r^2(\partial\overline{\Delta n}/\partial r)dr \qquad (12)$$

where $\partial\overline{\Delta n}/\partial r$ is the refractive index increment gradient term which is directly proportional to the height of the boundary curve as measured from the base line (54). Equation (12) is derived assuming that the refractive index of the solution is a linear function of the solution concentration and that the specific refractive index increment is the same for all solute components. These conditions have been shown to be satisfied in the polystyrene – cyclohexane system (55,56).

Pressure Correction

Fujita (49) has generalized Equations (11) and (12) to correct for the effect of pressure in a compressible solvent, such as cyclohexane. This correction is necessary because the hydrostatic pressure in the liquid at the bottom of a centrifuge cell at 56,100 r.p.m. will be of the order of several hundred atmospheres. At these pressures the sedimentation of the polymer will be different than near the top of the cell where the pressures are close to one atmosphere.

The treatment by Fujita has been modified to a working form by Blair and Williams (57), and the following equations were used to calculate the corrected sedimentation coefficient, S', and the corresponding corrected weight distribution function, $G^*(S)$.

$$S_i' = (1/\omega_f^2 t_e) \left\{1 - \mathcal{K}[(r_i/r_o)^2 - 1)]\right\}/\ln(r_i/r_o) \qquad (13)$$

$$G^*(S_i) = r_i \omega_f^2 t_e \left\{1 - 2\mathcal{K}[(r_i/r_o)^2 - 1]\right\} (\partial\overline{\Delta n}/\partial r)_i / \int_o^\infty (\partial\overline{\Delta n}/\partial r)_i dr \qquad (14)$$

where $\mathcal{K}$, the pressure dependence parameter, takes the form

$$\mathcal{K} = 0.25\ \mu\ \omega_f^2\ \rho_o r_o^2 \qquad (15)$$

where ρ_o is the density of the solvent and μ is a constant characteristic of the solvent-solute pair. Billick (58) and Wales and Rehfeld (59) have experimentally evaluated the constant, μ, and found it to be in good agreement with the theoretical value of 2.0×10^{-4}. This value of μ was employed in Equation (15) to evaluate the pressure parameter, $\mathcal{K}$, for this study.

Diffusion Correction

The pressure-corrected apparent distributions were corrected for diffusion effects by an extrapolation of the distribution to infinite time. Gosting (60) has shown that at infinite time the effects of diffusion become small with respect to the boundary-spreading effects of polymolecularity. The method of extrapolation is one that was suggested by Baldwin (61) and used by Emery (22).

The method involves the extrapolation of $\underline{S}$ against a reciprocal time function $\underline{t}_e \exp(\bar{\underline{S}}_1' \omega_f \underline{t}_e)$ for fixed values of $\underline{G}^*(\underline{S})/\underline{G}^*(\underline{S})_{max}$, where $\bar{\underline{S}}_1'$ is the first moment of the pressure-corrected distribution. The extrapolated values of $\underline{S}'$ and $\underline{G}^*(\underline{S})/\underline{G}^*(\underline{S})_{max}$ are the diffusion-corrected distribution. The ordinate of the distribution, $\underline{G}^*(\underline{S})/\underline{G}^*(\underline{S})_{max}$, is then multiplied by $\underline{G}^*(\underline{S})_{max}$ to obtain the diffusion-free distribution of $\underline{G}(\underline{S})$ versus $\underline{S}^o$.

Concentration Correction

The sedimentation velocity method for determining the sedimentation coefficient distribution assumes that $\underline{S}$ is independent of concentration. This condition is satisfied at infinite dilution; however, the analyses were made at a finite dilution. It is, therefore, necessary to correct the distributions to infinite dilution.

An analytical method of extrapolating the distributions to infinite dilution was selected over graphical extrapolation techniques because of the extensive amount of experimental work required by the latter method. Cantow (62) has experimentally defined a relationship for the polystyrene – cyclohexane system which relates the dependence of the sedimentation coefficient at infinite dilution, S, to the diffusion-corrected coefficient, S^o, and the concentration, C, as follows:

$$S^o = S/(1 + 0.006\ S^2C_v^2) \qquad (16).$$

This relationship was also used by Emery (22) and further details of the calculation are given there.

EXPERIMENTAL DATA AND DISCUSSION OF RESULTS

REVERSIBILITY STUDIES

It will be recalled that the criterion for reversibility was that the final equilibrium state of the system be independent of the path to that state. In this study, reversibility was studied with respect to molecular weight by varying the sequence of addition of narrow molecular weight distribution samples to the system while attaining the same final conditions in the system.

TWO POLYMER SYSTEM

Experimental

Two narrow molecular weight distribution polystyrene samples, PS103 and PS108 (see Table I), were used in the reversibility experiments. Fifteen milliliters of PS103 and 15 ml. of PS108 were added to tubes containing 2.0 g. of carbon black. In a third tube, 15 ml. of both PS103 and PS108 were also added to 2.0 g. of carbon black. After equilibration for 4 days, 15 ml. of PS108 were added to the PS103 tube and 15 ml. of PS103 were added to the PS108 tube. The tube containing the mixture of the two polymer samples was not opened. The three tubes were then equilibrated for an additional 4 days. At the end of the second equilibration time, all three tubes were opened and the intrinsic viscosity of each bulk phase was determined. The above experiments were repeated at several concentration levels of PS103 and PS108. Table VII presents a summary of the polymer solutions used and the calculated intrinsic viscosity, $[\eta]_{oc}$, obtained for the mixture of PS103 and PS108.

TABLE VII

SOLUTIONS USED IN THE TWO POLYMER REVERSIBILITY SYSTEMS

	Polymer PS103		Polymer PS108		Polymers PS103 & PS108	
Set	Concn., g./dl.	$[\eta]_o$, dl./g.	Concn., g./dl.	$[\eta]_o$, dl./g.	Concn., g./dl.	$[\eta]_{oc}$, dl./g.
I	0.678	0.469	0.243	0.771	0.468	0.549
II	0.434	0.469	0.438	0.771	0.436	0.621
III	0.242	0.469	0.682	0.771	0.461	0.692

Results

Emery (22) and Kolthoff and Gutmacher (9) have demonstrated that polymer exchange can occur between the bulk and surface phases in an adsorption system. By using nearly duplicate samples, the only difference being the order of addition of the polymers, it was possible in this study to demonstrate that the same equilibrium state may be obtained by different paths. The data from these samples are presented in Table VIII.

TABLE VIII

SUMMARY OF REVERSIBILITY EXPERIMENTS FOR THE TWO POLYMER SYSTEM

Set No.	Tube No.	Polymer Added at Zero Time	Polymer Added After 4 Days	Equilibrium Condition $[\eta]_B$, dl./g.	Equilibrium Condition Γ, mg./g.
I	1	PS103	PS108	0.524	13.1
	2	PS103 & PS108	--	0.523	13.0
	3	PS108	PS103	0.525	13.7
II	4	PS103	PS108	0.589	13.9
	5	PS103 & PS108	--	0.594	14.4
	6	PS108	PS103	0.587	14.0
III	7	PS103	PS108	0.669	15.0
	8	PS103 & PS108	--	0.670	15.1
	9	PS108	PS103	0.668	14.8

The nearly identical intrinsic viscosity values within a set of experiments give good evidence that the system attained the same equilibrium state by different paths. As expected, when different proportions of the two polymers were used, different values of the intrinsic viscosity and the specific adsorption were obtained at equilibrium. The data demonstrate that the equilibrium state of this system is independent of the path, but dependent on the final conditions of the system.

THREE POLYMER SYSTEM

In this section, the study of the reversibility of a two-polymer system was extended to a three-polymer system.

Experimental

The three narrow molecular weight distribution polymers used in the following experiments were PS103, PS108, and PL10, and their respective solution concentrations were 0.412, 0.399, and 0.397 g./dl. Several adsorption tubes were prepared with 2.0 g. of carbon black in each tube. To one of the tubes, 10 ml. of one of the three polymer solutions were added, and the tube was sealed and mounted on the rotator. After 4 days, the tube was opened, 10 ml. of the second of the three polymer solutions were added and the tube was equilibrated for an additional 4 days. Then 10 ml. of the third solution were added and the 30 ml. of solution equilibrated for 4 days. The isolated bulk phase was then analyzed to determine its intrinsic viscosity. This procedure was repeated for each of the tubes tested, but the order of addition of polymer solutions to each tube was varied. In one tube, the three polymer solutions were added simultaneously and equilibrated for 12 days.

Results

The summary of the results from the three-polymer system is presented in Table IX.

TABLE IX

SUMMARY OF REVERSIBILITY EXPERIMENTS FOR THE THREE-POLYMER SYSTEM

Tube No.	Polymer Added at Zero Time	Polymer Added After 4 Days	Polymer Added After 8 Days	Equilibrium Condition $[\eta]_B$, dl./g.	Equilibrium Condition Γ, mg./g.
1	PS108	PL10	PS103	0.751	16.1
2	PS108	PL10	PS103	0.746	16.3
3	PS108	PS103	PL10	0.749	16.3
4	PL10	PS108	PS103	0.735	16.2
5	PL10	PS108	PS103	0.734	16.1
6	PL10	PS108	PS103	0.740	16.1
7	PS103, PS108 & PL10	--	--	0.741	16.5

These results demonstrate that the equilibrium state is independent of order of addition of the polymer samples to a system when the final condition of the systems are equivalent. The results were analyzed statistically with the t-test (63) and were not found to be significantly different at the 95% confidence level.

DISCUSSION OF REVERSIBILITY STUDIES

The results of the two and three-polymer systems demonstrated that the order of addition of the polymer samples to the system did not affect the final equilibrium state of the system. This can also be stated: the equilibrium state is independent of the path to that state for this system. Therefore, the system can be considered to be reversible with respect to molecular weight effects.

Evidence has been presented previously (see the Introduction) that polymer adsorption is reversible with respect to solvent, temperature, and concentration. These results, together with the reversibility data presented in this study, demonstrate that this polymer system satisfies the reversibility criterion of thermodynamic equilibrium.

The assumption of thermodynamic equilibrium has been made in the theoretical papers dealing with polymer adsorption, and the reversibility data presented here and in the literature support this assumption. Thermodynamic equilibrium requires that the chemical potential of each component in the bulk and surface phases be equal. Therefore, with a polydisperse polymer, each polymer homologue must be partitioned between the bulk and surface phases. Since each homologue is readily identified by its degree of polymerization, D.P., there should exist a relationship between the partitioning of the polymer and its D.P. Emery (22) determined a partitioning relationship for his system, and it was a purpose of this work to obtain additional information of the partitioning of polymers at equilibrium.

EQUILIBRIUM ADSORPTION BEHAVIOR OF POLYDISPERSE POLYMERS

Equilibrium adsorption experiments were performed with two polydisperse polymers. These experiments were made under a variety of experimental conditions to investigate the adsorption characteristics of the system and the effect of different original polymer distributions. Several of the bulk phase samples were selected for ultracentrifuge analysis to determine their molecular weight distributions.

INTRINSIC VISCOSITY AND RELATED STUDIES

Experimental

The equilibrium adsorption behavior of Polystyrenes PB5 and PB6 were studied for different ratios of adsorbent weight to solution volume over a range of

solution concentrations. Solution volumes of 15 and 30 ml. were used, the adsorbent weight was varied between 0.5 and 5.0 g., and the solution concentrations were varied from 2.5 to 7.0 mg./cc. Following equilibration at 25.0°C. for 4 days, the intrinsic viscosity of the bulk phase samples was determined.

Adsorption Isotherms

Several investigators (14,15,64) have found polymer adsorption isotherms of the Langmuir type, and recently Emery (22) has shown that the Langmuir isotherm fits the adsorption data for a system similar to the present one. The use of this type of isotherm has been criticized on theoretical grounds by Silberberg (2) and recently by Hoeve (7). The basis of the criticism is that a polymer system should not attain a limiting specific adsorption value as predicted by the Langmuir isotherm. However, the Langmuir isotherm has been found to fit polymer adsorption data over a wide range of solution concentrations, and, in the present study, the adsorption isotherms were found to be of the Langmuir type.

The Langmuir isotherm may be written in linear form as follows:

$$C_v/\Gamma = C_v/\Gamma_m + 1/K\Gamma_m \qquad (17)$$

where Γ is the specific adsorption, i.e., the weight of adsorbed polymer per unit weight of adsorbent, C_v is the equilibrium concentration, K is an equilibrium constant, and Γ_m is the maximum or limiting specific adsorption. Figures 2 and 3 present the adsorption results plotted in the form of Equation (17). A linear regression analysis of the data yielded the following values: a correlation coefficient of 0.992, Γ_m = 14.9 mg./g., and K = 9.72 cc./mg. for Polystyrene PB5 and a correlation coefficient of 0.997, Γ_m = 16.2 mg./g., and K = 13.6 cc./mg. for Polystyrene PB6.

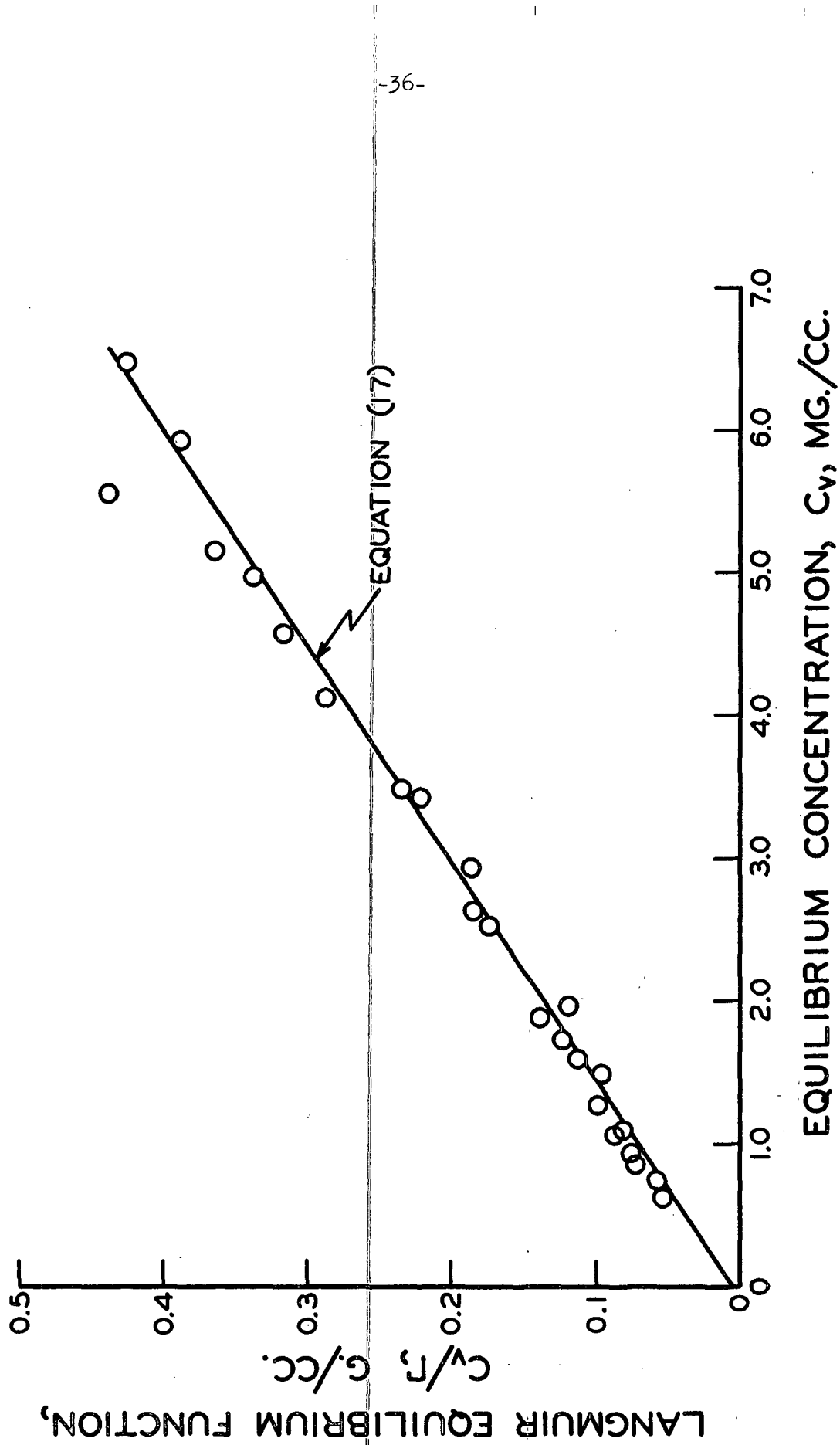

Figure 2. Langmuir Plot for Polystyrene PB5

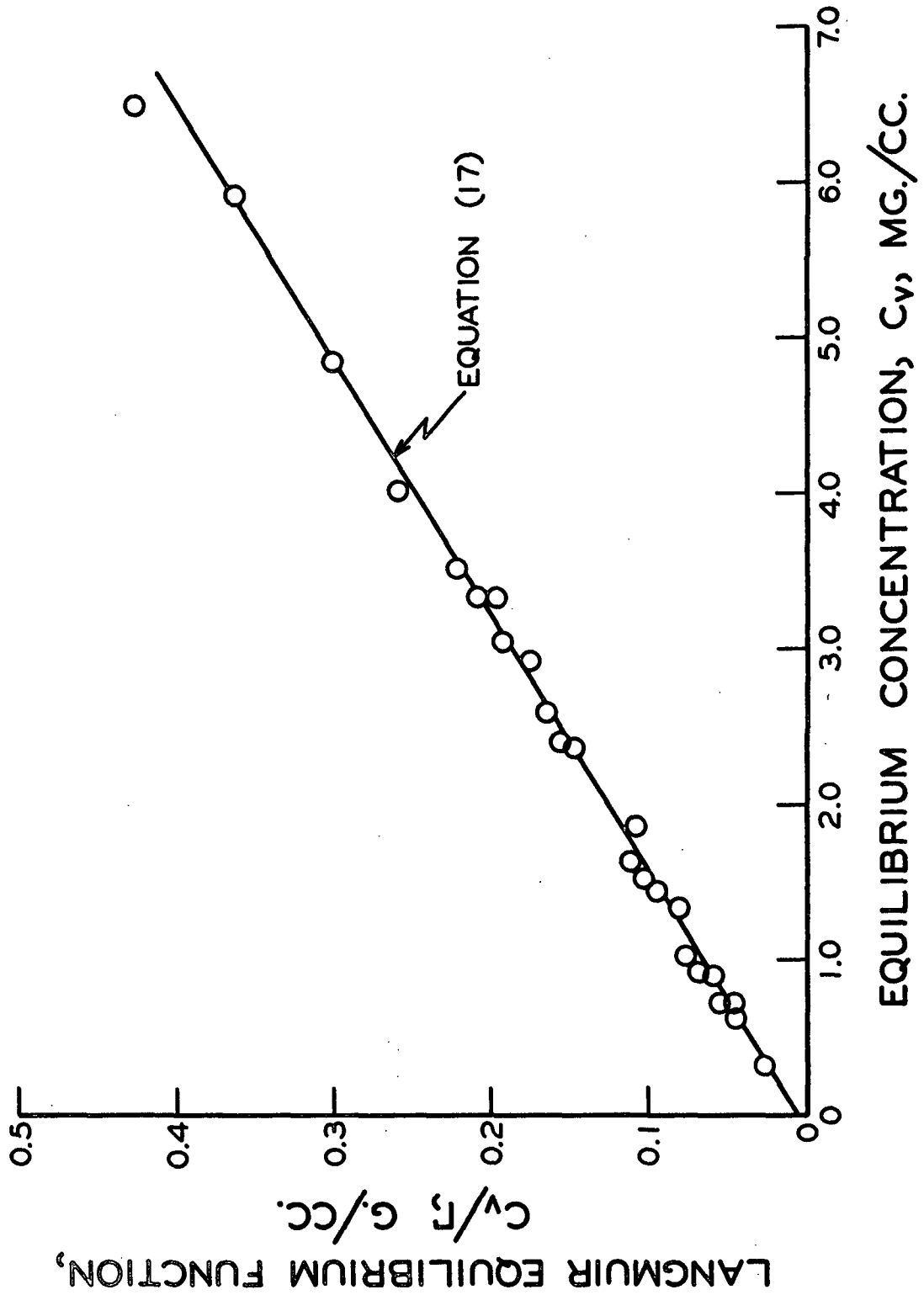

Figure 3. Langmuir Plot for Polystyrene PB6

From the constants, Γ_m and K, the adsorption isotherms may be computed with Equation (18), a rearranged form of Equation (17).

$$\Gamma = K \Gamma_m C_v / (1 + KC_v) \qquad (18).$$

Figures 4 and 5 present these isotherms and the adsorption data for Polystyrene PB5 and PB6, respectively. These figures demonstrate that the isotherms level off at very low solution concentrations. This has been previously noted in both experimental (14,22,62) and theoretical (2,7) analyses.

The calculated maximum specific adsorption for PB6 was found to be greater than that for PB5. Qualitatively this agrees with the theoretical discussions by Hoeve (7) and Silberberg (2) where it was found that the tendency of the isotherm to level off occurs at higher values of the specific adsorption, the higher the molecular weight. Although the quantity, Γ_m, theoretically may have limited significance, it provides a measure of the value of the specific adsorption where the isotherm has tended to level off.

Fractionation Behavior in the Bulk Phase

Analyses of the bulk phases from the adsorption experiments show that the intrinsic viscosity values for this phase may be represented by a single parameter, the weight fraction of polymer adsorbed. Figures 6 and 7 illustrate the relationship between intrinsic viscosity of the bulk phase and the weight fraction of polymer adsorbed for the polystyrene Samples PB5 and PB6, respectively.

The weight fraction of polymer adsorbed, X_A, may be expressed in terms of the equilibrium concentration, C_w, and the original solution concentration, C_o as follows:

$$X_A = 1 - C_w/C_o \qquad (19).$$

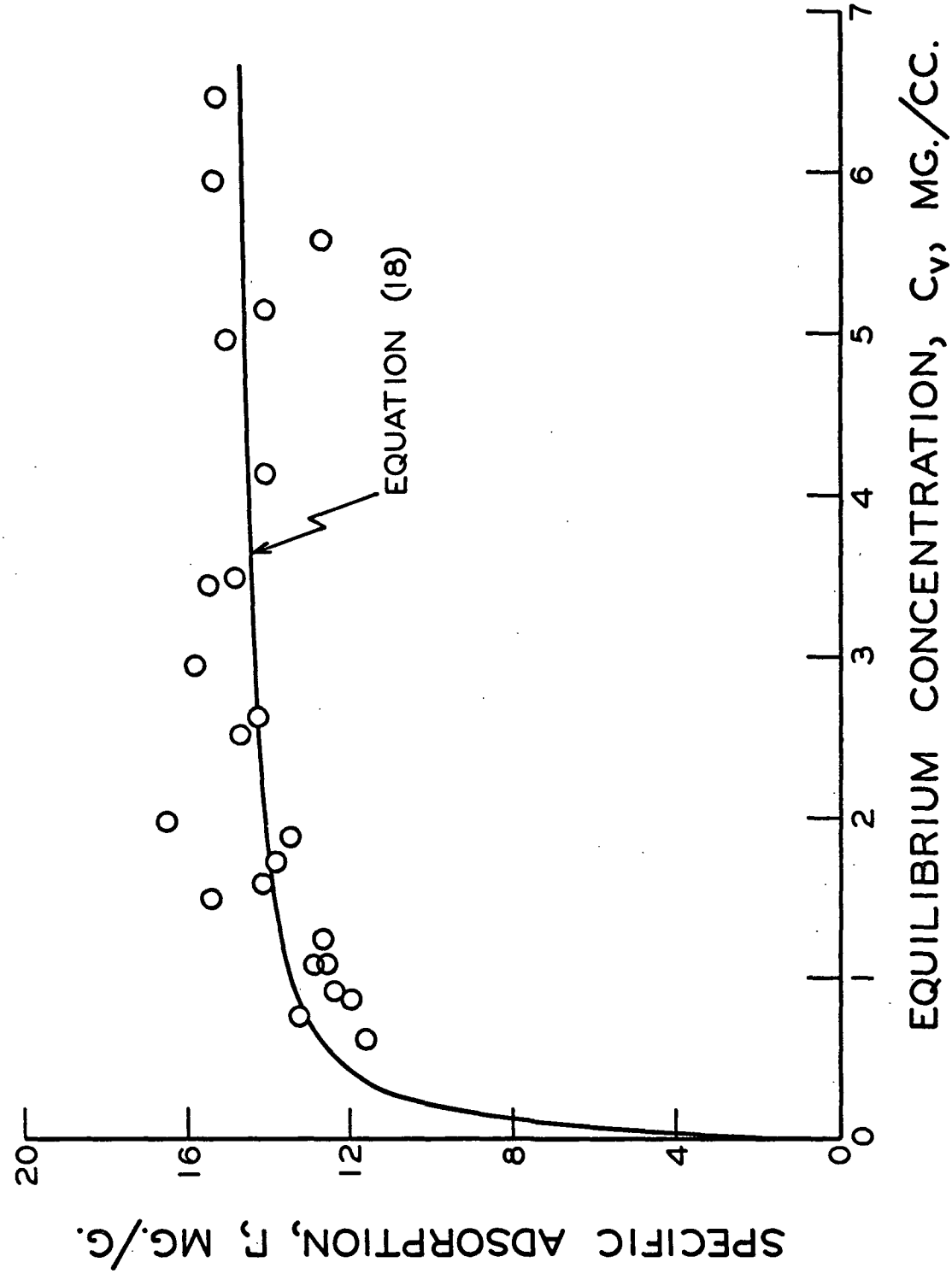

Figure 4. Langmuir Adsorption Isotherm for Polystyrene PB5

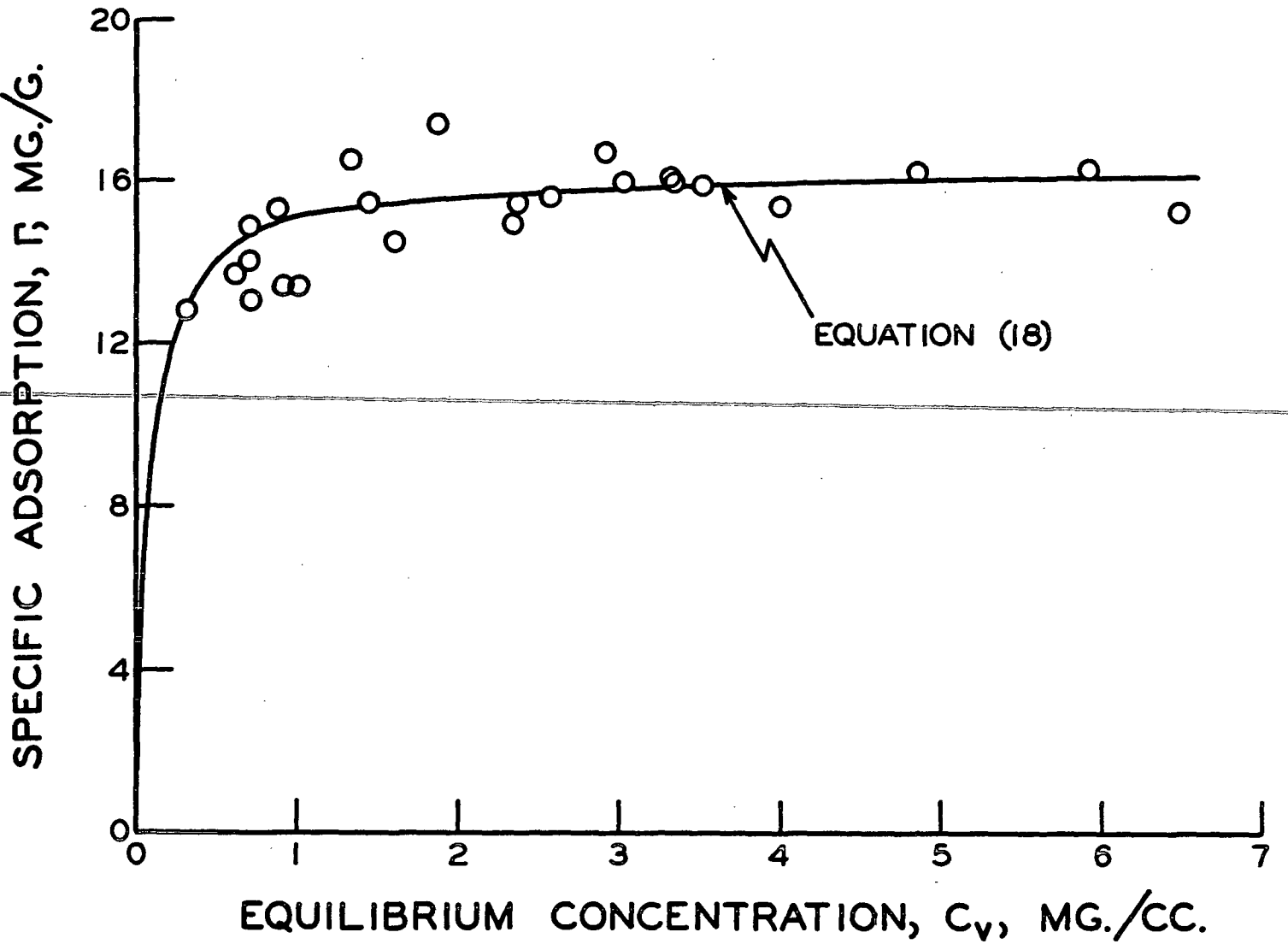

Figure 5. Langmuir Adsorption Isotherm for Polystyrene PB6

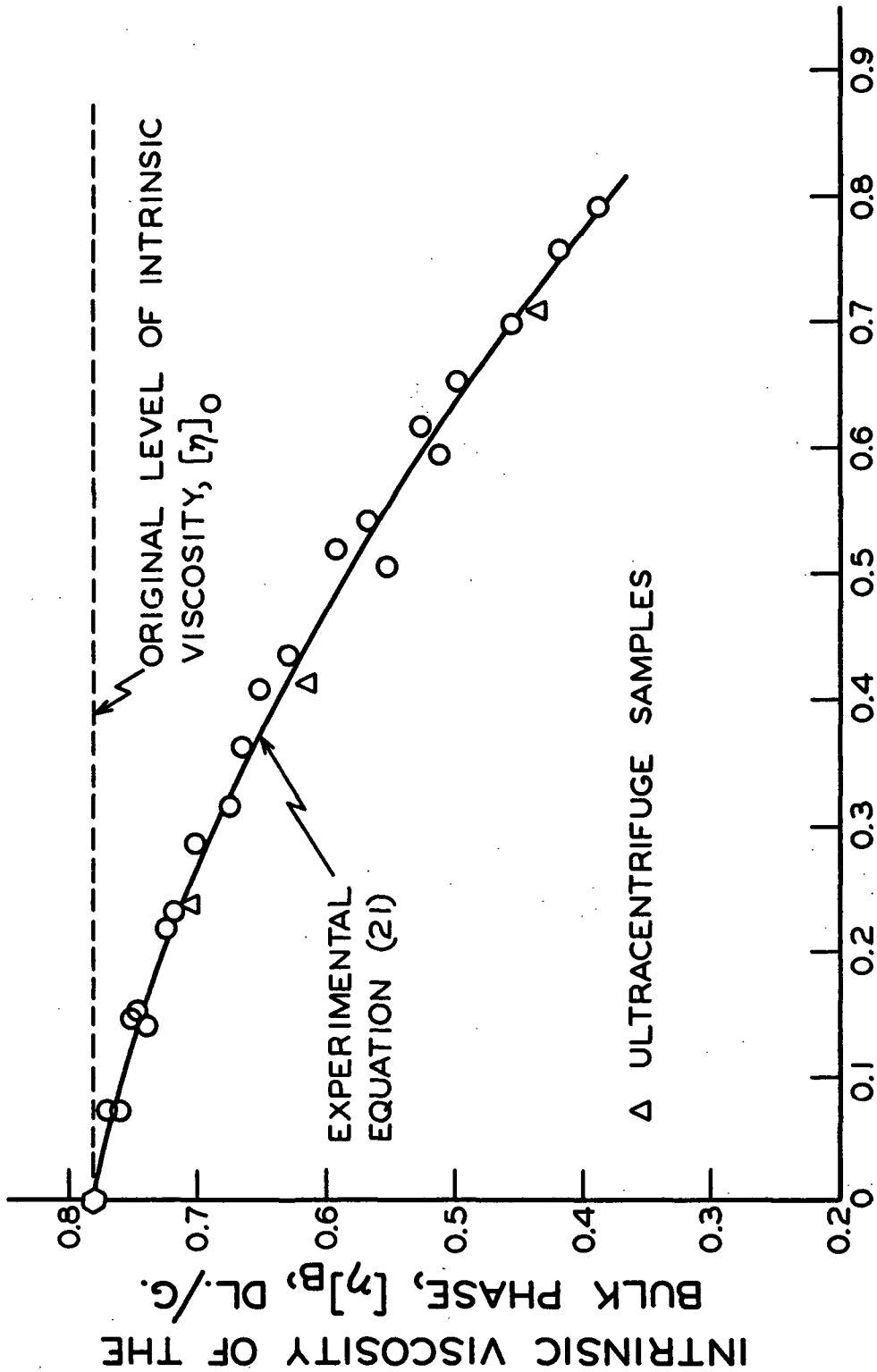

Figure 6. Equilibrium Fractionation Behavior of Polystyrene PB5 in the Bulk Phase

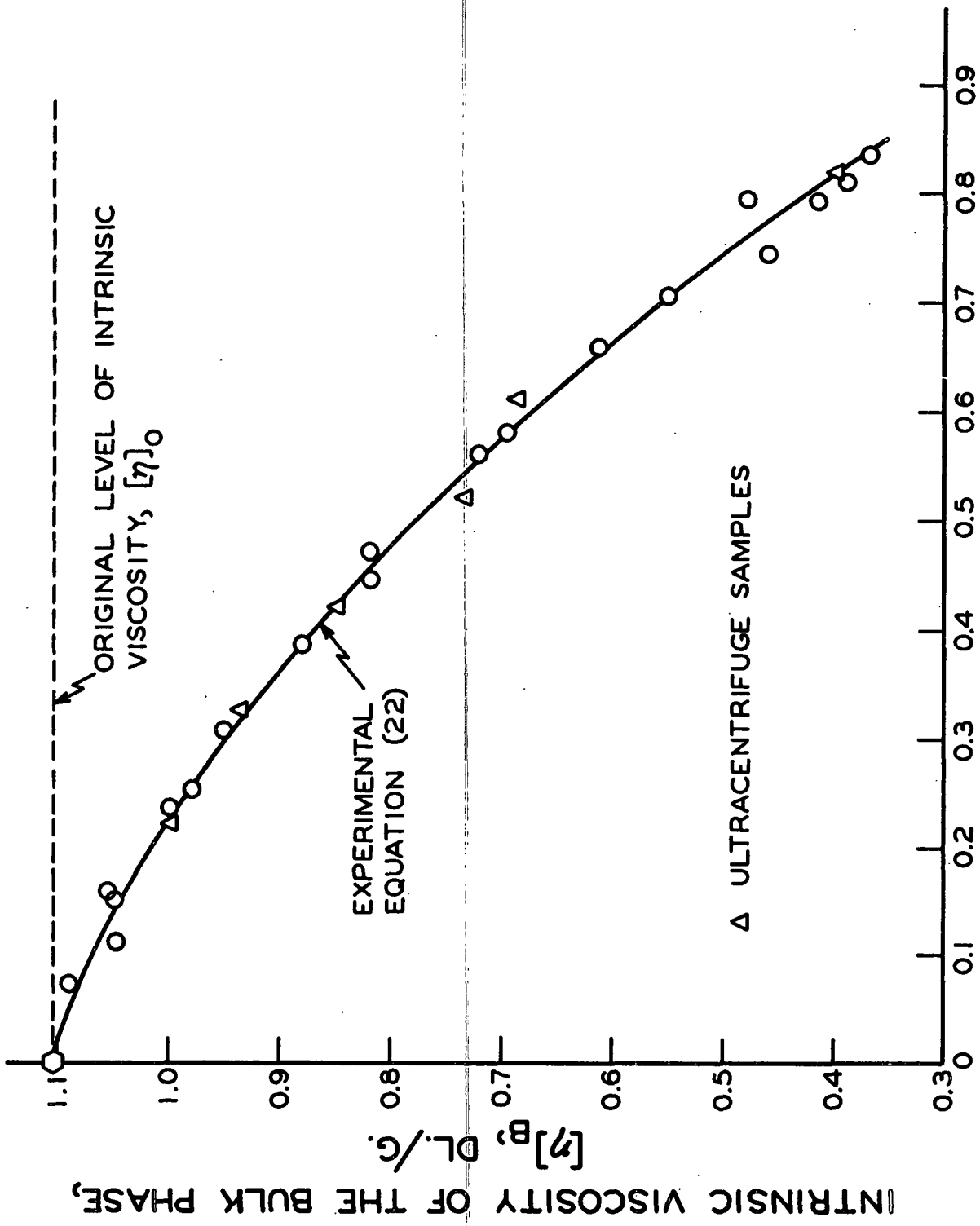

Figure 7. Equilibrium Fractionation Behavior of Polystyrene PB6 in the Bulk Phase

An alternative expression for $\underline{X_A}$ in terms of the experimental variables is given by Equation (20)

$$X_A = \Gamma W_A / C_o V \tag{20}$$

where Γ is the specific adsorption, $\underline{W_A}$ is the weight of adsorbent, and $\underline{V}$ is the volume of solution. It is readily seen that Equations (19) and (20) are equivalent relationships.

Experimentally, both $\underline{W_A}$ and $\underline{C_o}$ were varied and $\underline{V}$ held constant to obtain the desired levels of $\underline{X_A}$. (The specific adsorption, Γ, was essentially constant in the range of equilibrium concentrations attained as shown in Fig. 4 and 5.) Equivalent levels of $\underline{X_A}$ could also have been obtained by variation of any single parameter while holding the others constant.

The results presented in Fig. 6 and 7 were evaluated statistically and found to be best fitted by second-order expressions with correlation coefficients in excess of 0.99. These equations for PB5 and PB6 are given, respectively, as follows:

$$[\eta]_B = 0.782 - 0.208(X_A) - 0.367(X_A)^2 \tag{21}$$

$$[\eta]_B = 1.104 - 0.310(X_A) - 0.676(X_A)^2 \tag{22}$$

where $[\eta]_{\underline{B}}$ is the bulk phase intrinsic viscosity. To guide the regression equation at low levels of $\underline{X_A}$ a constraint, $[\eta]_o$, the intrinsic viscosity of the original solution, was used at $\underline{X_A} = 0$. The data were analyzed with and without the constraint and the goodness of fit was not found to be altered significantly.

If no fractionation of the polymer occurred on adsorption, the dotted curve in Fig. 6 and 7 would represent the intrinsic viscosity at all levels of $\underline{X_A}$.

With no fractionation, there would not be a change in the molecular weight distribution of the polymer in the bulk phase during adsorption and the intrinsic viscosity would remain constant at $[\eta]_o$.

Since the intrinsic viscosity of the bulk phase did not remain constant at $[\eta]_o$, the molecular weight distribution of the bulk phase did not remain constant. Although a single parameter, such as intrinsic viscosity, does not characterize the distribution, the decrease of intrinsic viscosity with increasing values of $\underline{X}_A$ indicates that preferential adsorption of the high molecular weight species was occurring. This does not necessarily indicate that only the high molecular weight species were removed from the bulk phase, but that the fraction of high molecular weight species removed was greater than the fraction of lower molecular weight species removed at any given level of $\underline{X}_A$.

Figures 6 and 7 show that the intrinsic viscosities of the bulk phase samples for both PB5 and PB6 decreased with increasing values of $\underline{X}_A$, but the decrease of intrinsic viscosity is more rapid with PB6 than PB5. This is also observed by considering the first and second-order coefficients of Equations (21) and (22). This results from the difference between the molecular weight distributions of the two-polymer samples. If the bulk phase intrinsic viscosity of a monodisperse polymer were plotted against the weight fraction of that polymer adsorbed, a curve would result which would be equivalent to the dotted curves plotted on Fig. 6 and 7 for no fractionation. As the molecular weight distribution spreads from monodisperse to polydisperse, fractionation effects would be observed, and the fractionation curve would deviate from the no-fractionation curve. Since PB6 is more polydisperse, $\underline{M}_w/\underline{M}_n = 2.46$ than PB5, $\underline{M}_w/\underline{M}_n = 1.97$, the fractionation curve for PB6 deviates more from the no-fractionation curve than PB5.

Fractionation Behavior in the Surface Phase

From the definition of intrinsic viscosity, its weight additivity may readily be demonstrated. Therefore, the intrinsic viscosity of the polymer in the surface phase, $[\eta]_A$, may be calculated according to:

$$[\eta]_A = ([\eta]_o - X_B[\eta]_B)/X_A \qquad (23)$$

where X_B is the weight fraction of polymer in the bulk phase. The quantity, $[\eta]_A$, is the intrinsic viscosity that the polymer in the surface phase would exhibit if the polymer were completely desorbed and dissolved in pure solvent.

Using Equation (23), the surface phase intrinsic viscosities were calculated. The calculated values are presented in Fig. 8 and 9 for Polystyrene PB5 and PB6, respectively. The solid curves shown in the figures were obtained by combining Equation (23) with Equations (21) and (22) to obtain the following respective equations:

$$[\eta]_A = 0.782 + 0.208X_B + 0.367X_AX_B \qquad (24)$$

$$[\eta]_A = 1.104 + 0.310X_B + 0.676X_AX_B \qquad (25)$$

for PB5 and PB6. This procedure was selected over a direct regression of the $[\eta]_A$ data because Equations (21) and (22) were guided in the low X_A-range by the constraint, $[\eta]_o$.

As in Fig. 6 and 7, the dotted lines in Fig. 8 and 9 represent the original levels of intrinsic viscosity, $[\eta]_o$. If no fractionation had occurred, then the $[\eta]_A$ quantities would be constant at $[\eta]_o$ for all levels of X_A. The deviation of the $[\eta]_A$ values from the no-fractionation curve demonstrates that fractionation of the polymer was occurring and also that the high molecular weight species were preferentially adsorbed.

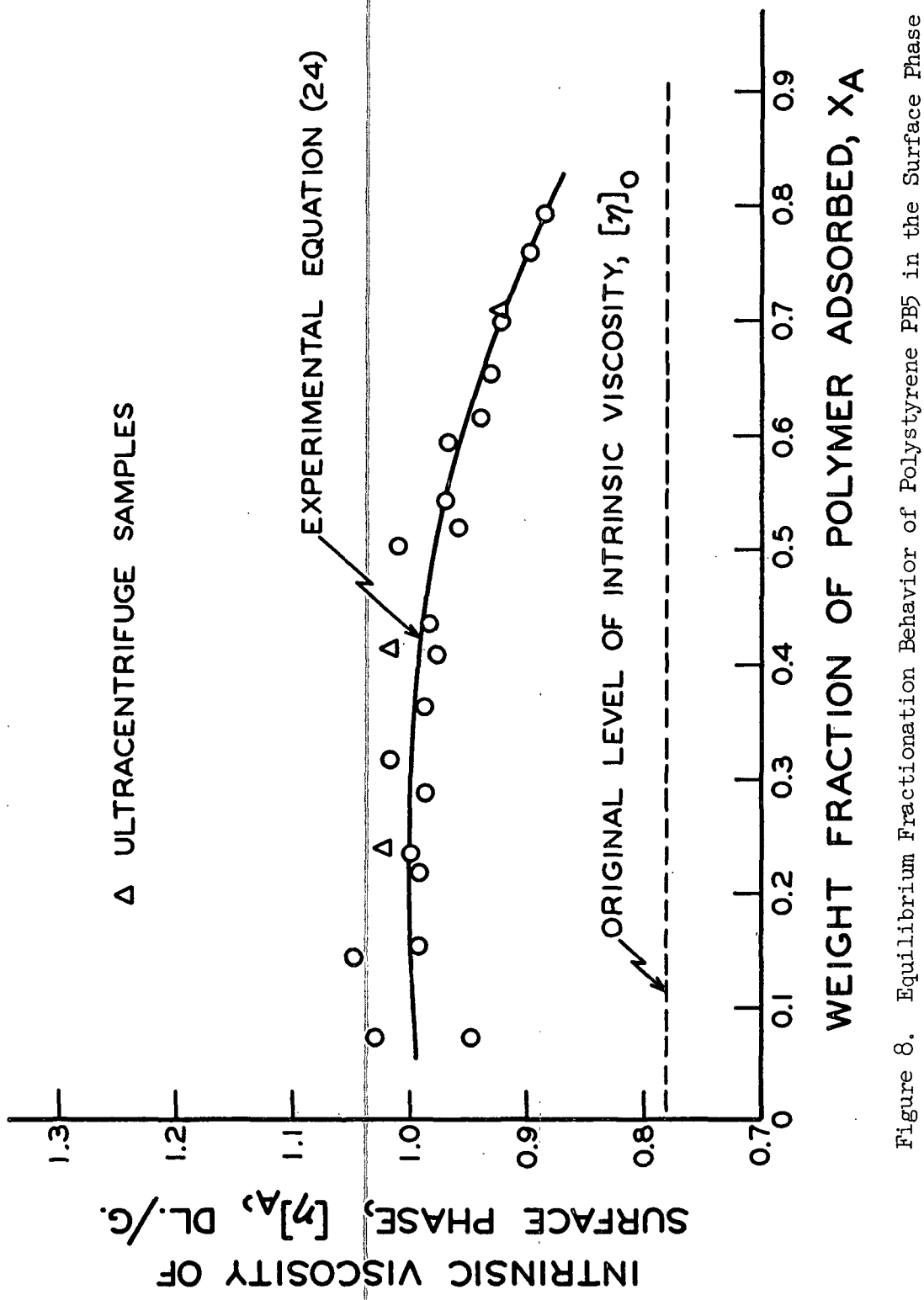

Figure 8. Equilibrium Fractionation Behavior of Polystyrene PB5 in the Surface Phase

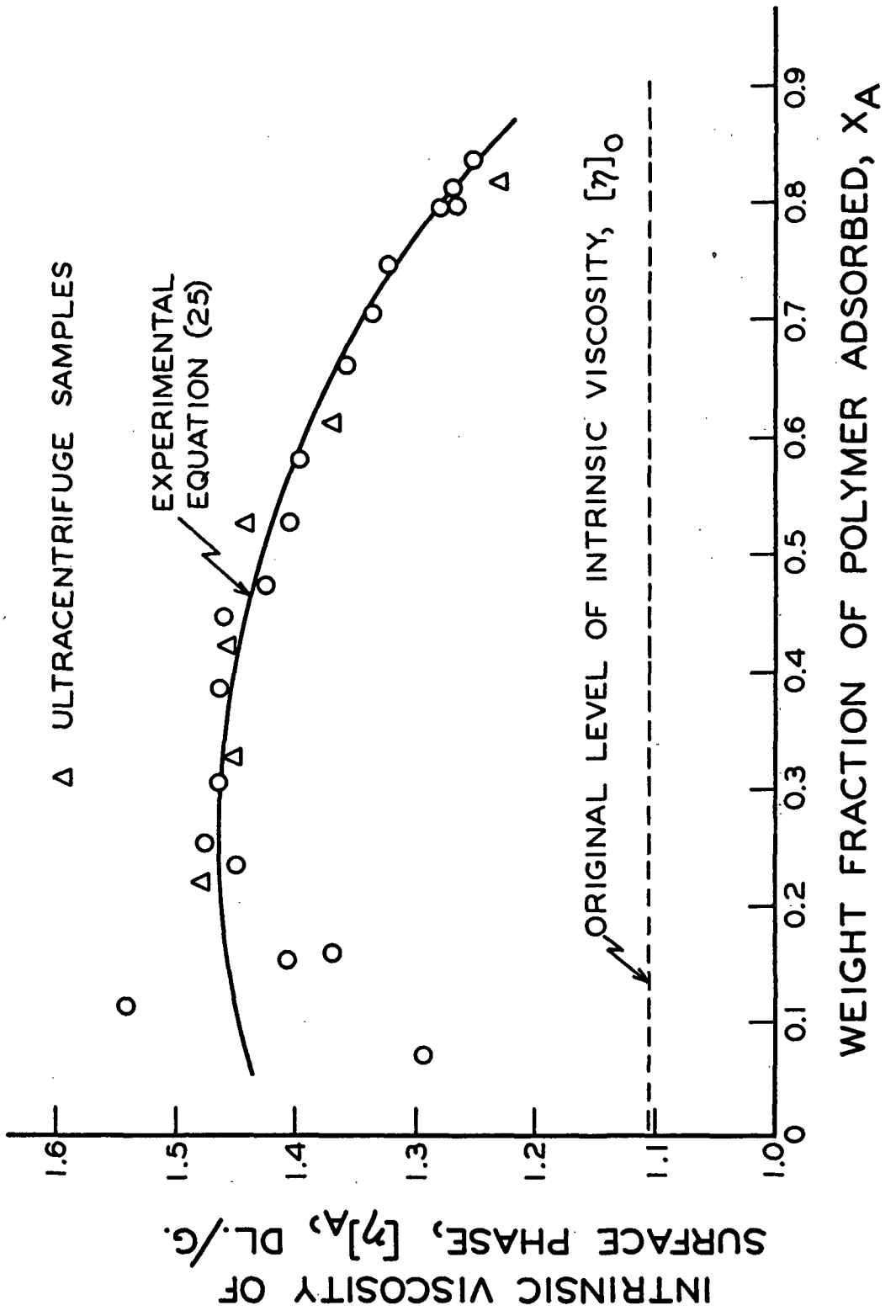

Figure 9. Equilibrium Fractionation Behavior of Polystyrene PB6 in the Surface Phase

In the region of low $\underline{X}_A$ values, $[\eta]_{\underline{A}}$ was found to remain nearly constant, Fig. 7 and 8. This behavior suggests that the distribution of polymers in the surface phase was established when there were excesses of all the polymer species in the bulk phase.

To further the understanding of the fractionation process, molecular weight distributions were determined before and after adsorption.

SEDIMENTATION VELOCITY STUDIES

Experimental

Sedimentation velocity experiments were made on Polystyrene PB5 and PB6 before adsorption and on the selected bulk phase samples indicated on Fig. 6 and 7.

For the adsorption experiments, the adsorbent weight was varied from 0.5 to 5.0 g., the solution concentrations were varied from 0.2 to 0.7 g./dl., and the solution volume was 30 ml. Following the equilibration period, four days, the supernatant solution was separated from the adsorbent. A portion of the solution was used for an intrinsic viscosity determination and the remaining sample was used for the sedimentation velocity study.

The samples used in the ultracentrifuge experiments were numbered according to the following four-digit scheme. The first digit indicates the original polymer sample, i.e., the digits 5 and 6 represent Polystyrene PB5 and PB6, respectively. The last two digits indicate the approximate value of the weight fraction of polymer adsorbed. The second digit indicates the ultracentrifuge run number for a particular sample (consecutive numbering began with the digit 0). For example, a sample number of 6020 shows that the original polymer was PB6, the weight fraction of polymer adsorbed was approximately 0.20, and the ultracentrifuge run was the first to be made on that sample.

The sedimentation velocity experiments were carried out in cyclohexane at 35.0°C., a theta solvent.

Sedimentation Coefficient Distributions

The sedimentation coefficient distributions of the Polystyrene Samples PB5 and PB6 before adsorption and the bulk phase samples after adsorption were determined directly from schlieren photographs. The sedimentation coefficient distributions of the surface phase samples were calculated from knowledge of the original and bulk phase distributions. It can be shown from a material balance that the differential weight distribution function of a sedimentation coefficient for the surface phase, $g_A(S)$, is given by the following:

$$g_A(S) = [g_o(S) - X_B g_B(S)] / \int_o^\infty [g_o(S) - X_B g_B(S)]\, dS \qquad (26)$$

where $g_B(S)$ and $g_o(S)$ are the distribution functions of the bulk phase and original distributions, respectively.

Distributions of sedimentation coefficients can be transformed to distributions of molecular weight from the following relationship (49):

$$g(S)dS = f(M)dM \qquad (27)$$

where $f(M)$ is the differential weight distribution function of the molecular weight, M. The sedimentation coefficient, S, may be related to the molecular weight, M, according to (65):

$$S = kM^b \qquad (28)$$

where k and b are constants which depend on the solvent-polymer pair and temperature. McCormick (66) has determined the coefficients k and b and reported values of 0.0169 and 0.48, respectively, for the polystyrene – cyclohexane system.

Equation (27) may be combined with Equation (28) to yield the differential weight distribution function of molecular weight:

$$f(M) = b(k)^{1/b}[S^{(b-1)/b}]g(S) \qquad (29).$$

The defining equations for the number, $\overline{M_n}$, and weight-average, $\overline{M_w}$, molecular weights are given, respectively, as follows:

$$\overline{M_n} = \int_0^\infty f(M)dM / \int_0^\infty [f(M)/M]\, dM \qquad (30)$$

$$\overline{M_w} = \int_0^\infty Mf(M)dM / \int_0^\infty f(M)dM \qquad (31).$$

The molecular weight averages may be expressed in terms of the sedimentation coefficient distributions by combining Equations (27) and (28) with Equations (30) and (31) as follows:

$$\overline{M_n} = k^{-1/b} \int_0^\infty g(S)dS / \int_0^\infty S^{-1/b} g(S)dS \qquad (32)$$

$$\overline{M_w} = k^{-1/b} \int_0^\infty Sg(S)dS / \int_0^\infty g(S)dS \qquad (33).$$

Using the above relationships, the average molecular weights determined for the ultracentrifuge samples are presented in Table X along with the first and second moments of the sedimentation coefficient distributions. The first and second moments, $\overline{S}_1$ and $\overline{S}_2$, respectively, are determined as follows:

$$\overline{S}_1 = \int_0^\infty Sg(S)dS / \int_0^\infty g(S)dS \qquad (34)$$

$$\overline{S}_2 = [\int_0^\infty S^2 g(S)dS / \int_0^\infty g(S)dS]^{1/2} \qquad (35).$$

Replicate determinations of the sedimentation coefficient distribution for Sample PB6 before adsorption were made and are presented in Fig. 10. Because the quality of photographs and the diffusion extrapolations were better for Sample 6300

TABLE X

SEDIMENTATION COEFFICIENT MOMENTS AND MOLECULAR WEIGHT AVERAGES CALCULATED FROM SEDIMENTATION COEFFICIENT DISTRIBUTIONS

Sample[a]	X_A	$\bar{S}_1$ Svedbergs	$\bar{S}_2$ Svedbergs	$\overline{M}_w \times 10^{-5}$	$\overline{M}_w/\overline{M}_n \times 10^{-5}$
Polystyrene PB6					
6300-0	0.0	7.94	8.59	4.39	2.46
6020-B	0.221	7.58	8.24	4.03	2.55
6020-S	0.221	9.45	9.90	5.88	1.54
6030-B	0.327	7.28	8.00	3.79	2.80
6030-S	0.327	9.31	9.74	5.68	1.60
6040-B	0.424	6.89	7.53	3.35	2.56
6040-S	0.424	9.37	9.83	5.80	1.66
6050-B	0.523	6.19	6.84	2.74	3.39
6050-S	0.523	9.34	9.80	5.76	1.58
6060-B	0.614	6.00	6.56	2.51	3.29
6060-S	0.614	9.08	9.60	5.52	1.88
6080-B	0.820	4.24	4.61	1.20	3.29
6080-S	0.820	8.68	9.19	5.04	1.78
Polystyrene PB5					
5100-0	0.0	6.68	7.13	2.98	1.97
5020-B	0.238	6.29	6.71	2.63	1.99
5020-S	0.238	7.95	8.32	4.10	1.51
5040-B	0.413	5.68	6.07	2.13	2.18
5040-S	0.413	8.02	8.36	4.13	1.43
5070-B	0.709	4.30	4.61	1.20	2.48
5070-S	0.709	7.49	7.82	3.61	1.46

[a] The letters O, B, and S, following the sample number indicate original polymer, bulk phase, and surface phase, respectively.

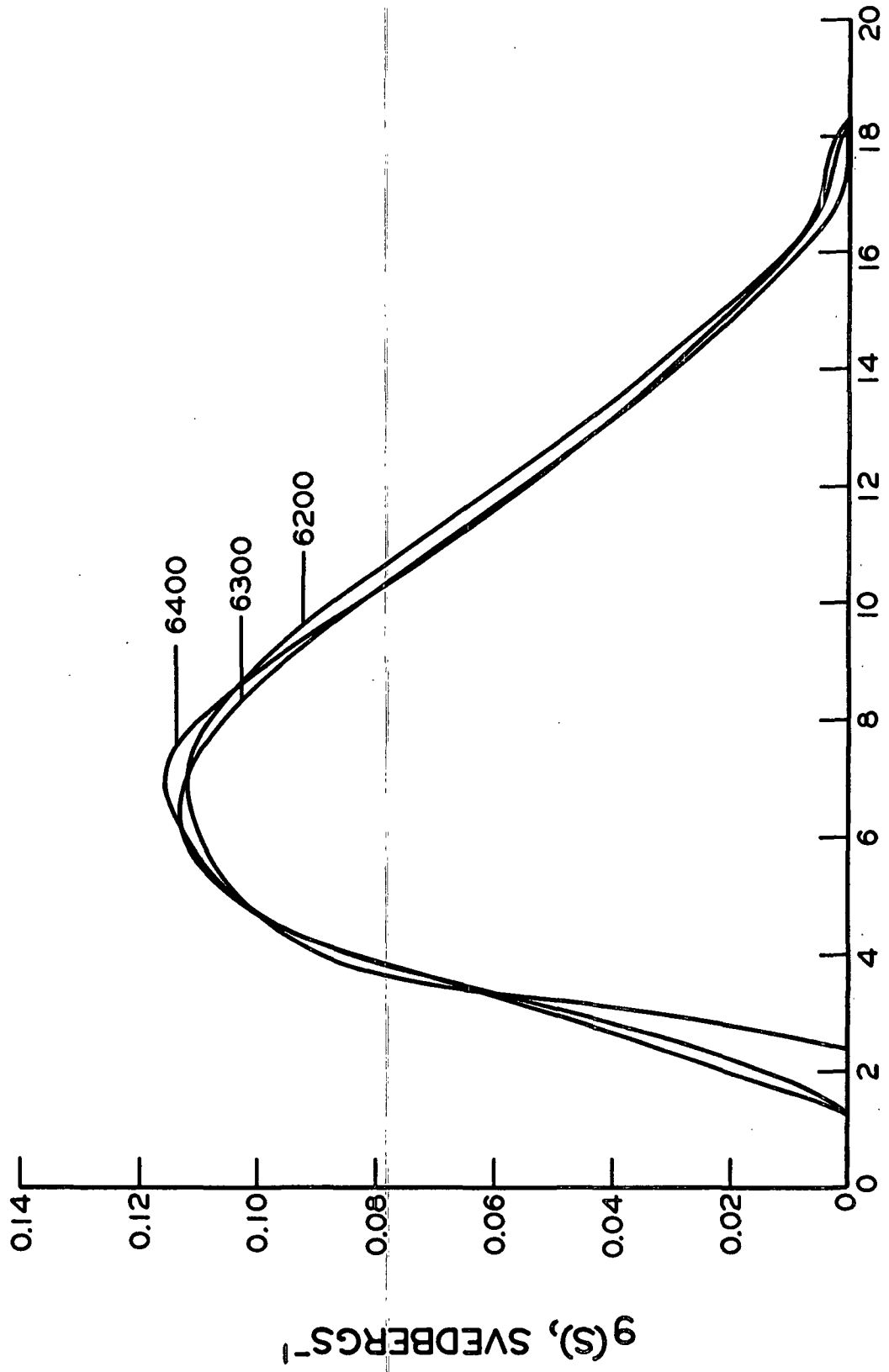

Figure 10. Comparison of Original Distributions for Polystyrene PB6

than with the other samples, the distribution obtained from that sample was used for the calculation of the surface phase distributions in Equation (26). The distribution obtained for Sample PB5 before adsorption is presented in Fig. 11.

A comparison of the bulk and surface phase sedimentation coefficient distributions for the adsorption experiments presented in Table X are given in Fig. 12-20. Figures 12-17 are for the distributions obtained from the adsorption experiments with Polystyrene PB6, and Fig. 18-20 are those from Polystyrene PB5.

It is readily apparent in Fig. 9-17 that fractionation of the polymer is occurring, and that the higher molecular weight polymers are preferentially adsorbed. It is recalled that the sedimentation coefficient is related to the molecular weight through Equation (28). These distributions confirm the viscometric results which indicated preferential adsorption of the higher molecular weight species. It may also be observed that more of the higher molecular weight species are adsorbed at high levels of $\underline{X_A}$ than at low.

The surface phase distributions from Fig. 12-15 have been replotted in Fig. 21 to demonstrate the consistency of these distributions at $\underline{X_A}$ values below 0.523 g./g. The adsorption results, Fig. 9, demonstrated that the intrinsic viscosity of the surface phase remained nearly constant at low levels of $\underline{X_A}$, and it was suggested from these data that the molecular weight distribution of polymer on the surface had become well established in this region. The surface-phase data presented in Fig. 21 demonstrate the consistency of these distributions that was indicated by intrinsic viscosity measurements. This is somewhat analogous, although in a greatly oversimplified way, to the plateau region of the Langmuir isotherm for gas adsorption where large changes of pressure in the gaseous phase have little effect on the amount of gas adsorbed per unit surface.

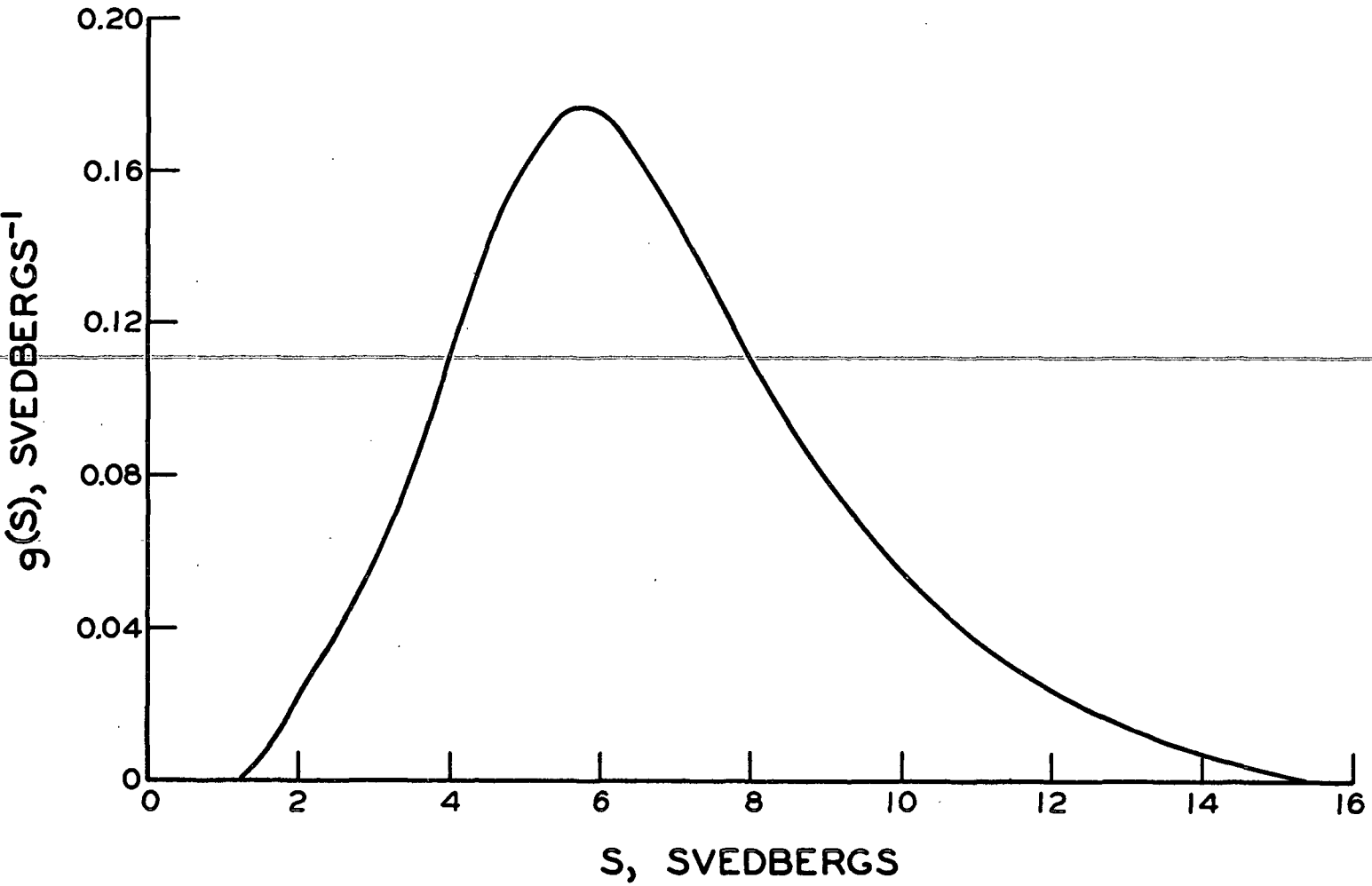

Figure 11. Original Distribution Determination for Polystyrene PB5

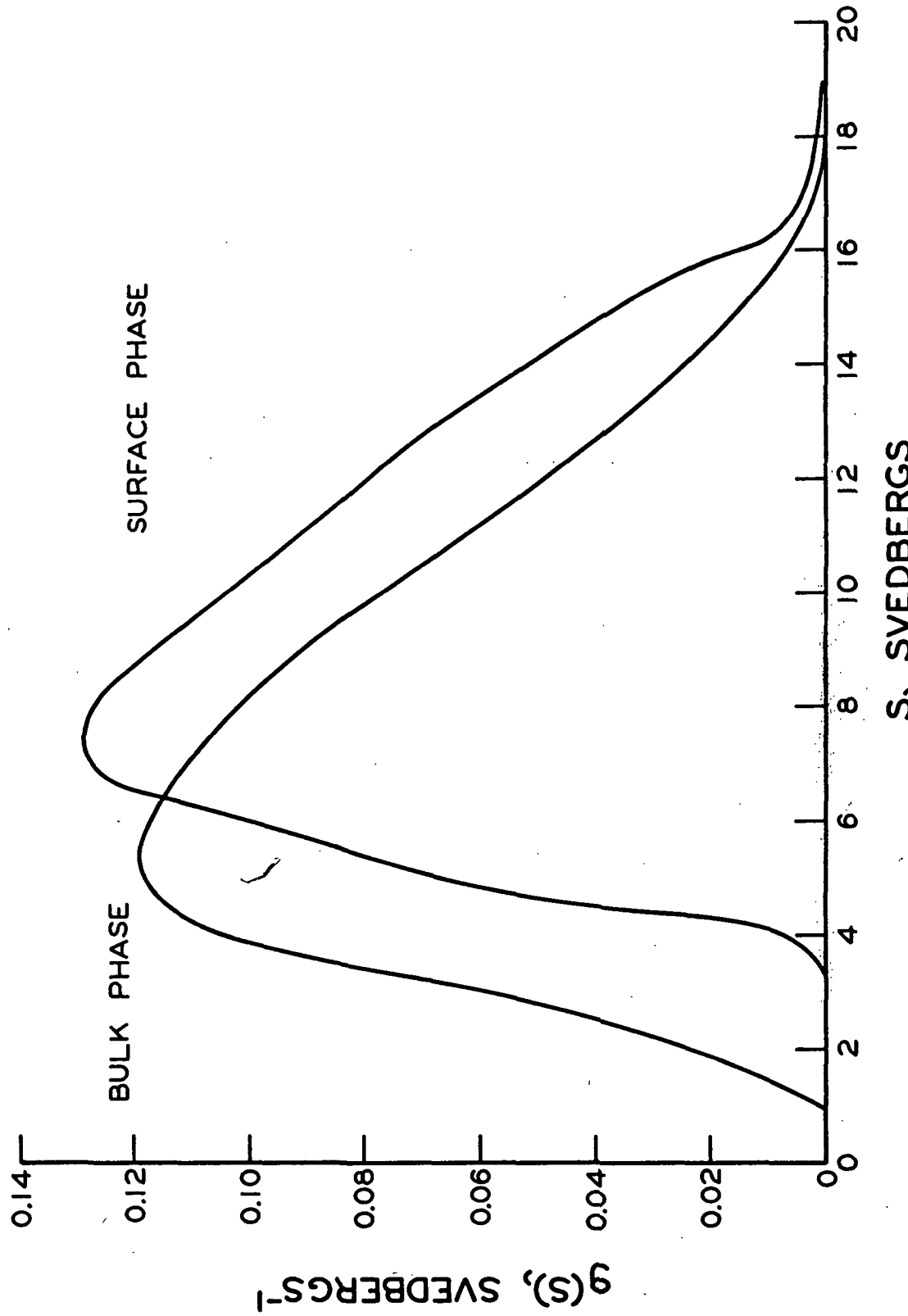

Figure 12. Normalized Distributions of Sedimentation Coefficients for Polystyrene PB6 Following Equilibrium Adsorption (Sample 6020)

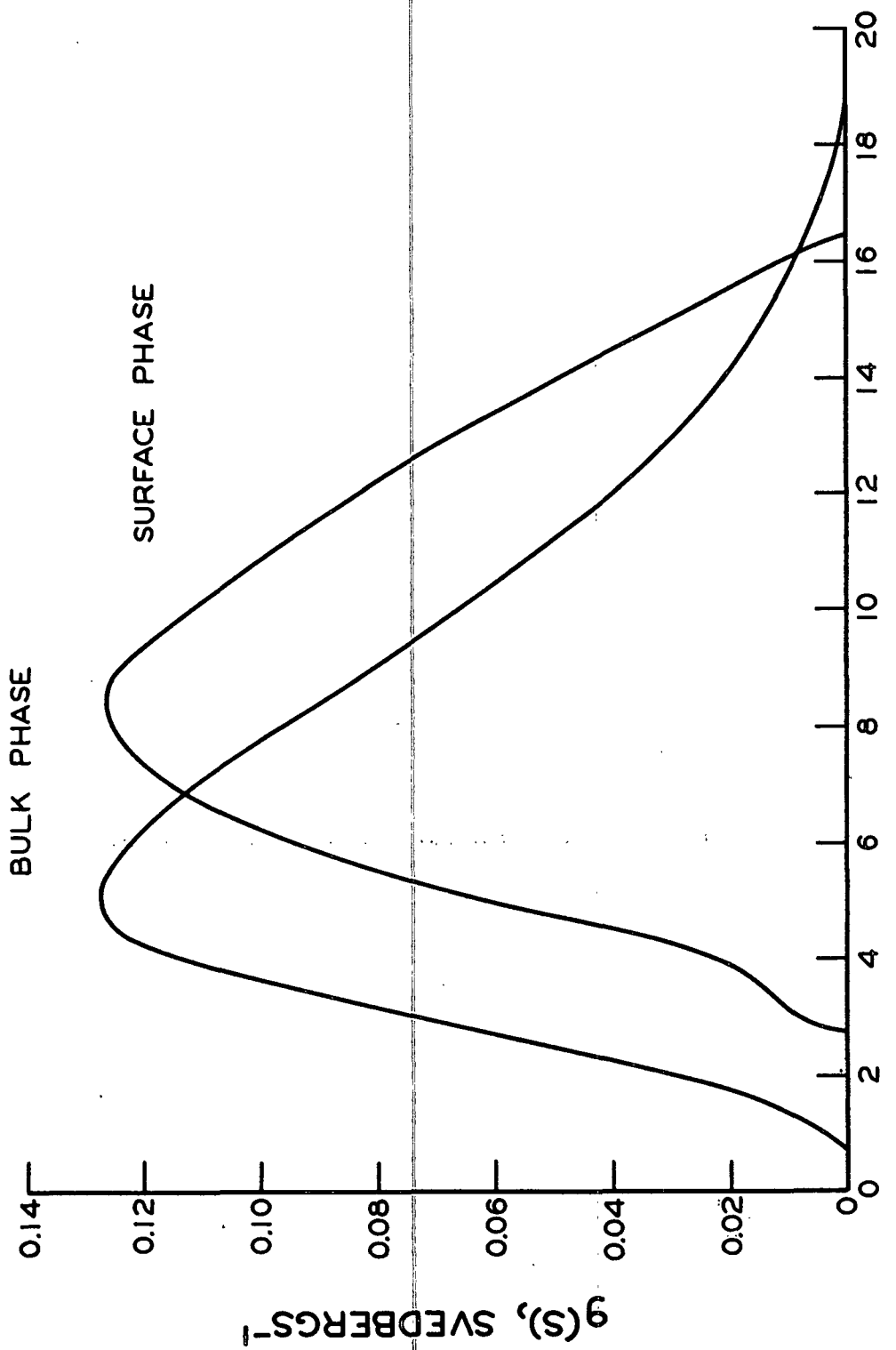

Figure 13. Normalized Distributions of Sedimentation Coefficients for Polystyrene PB6 Following Equilibrium Adsorption (Sample 6030)

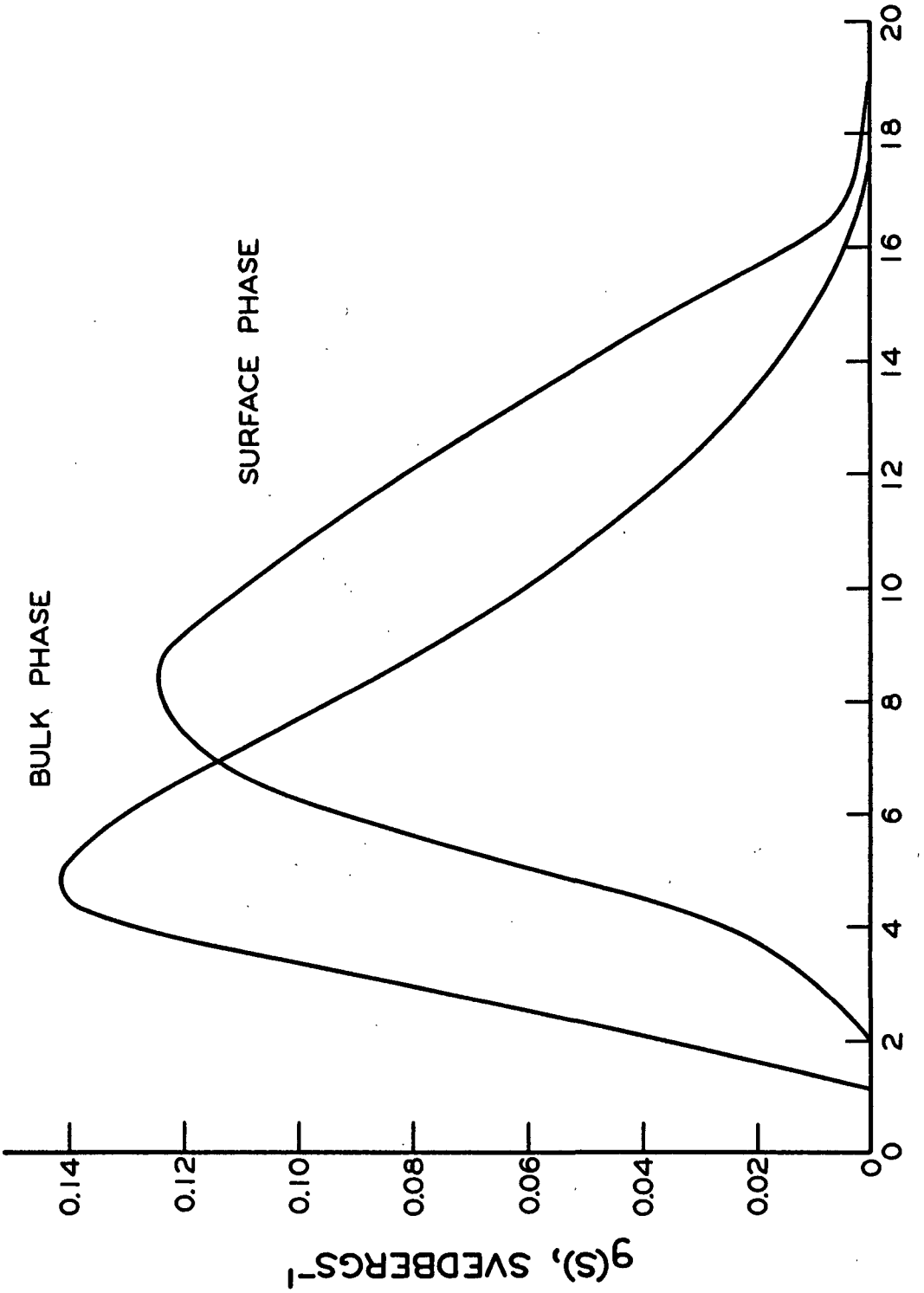

Figure 14. Normalized Distributions of Sedimentation Coefficients for Polystyrene PB6 Following Equilibrium Adsorption (Sample 6040)

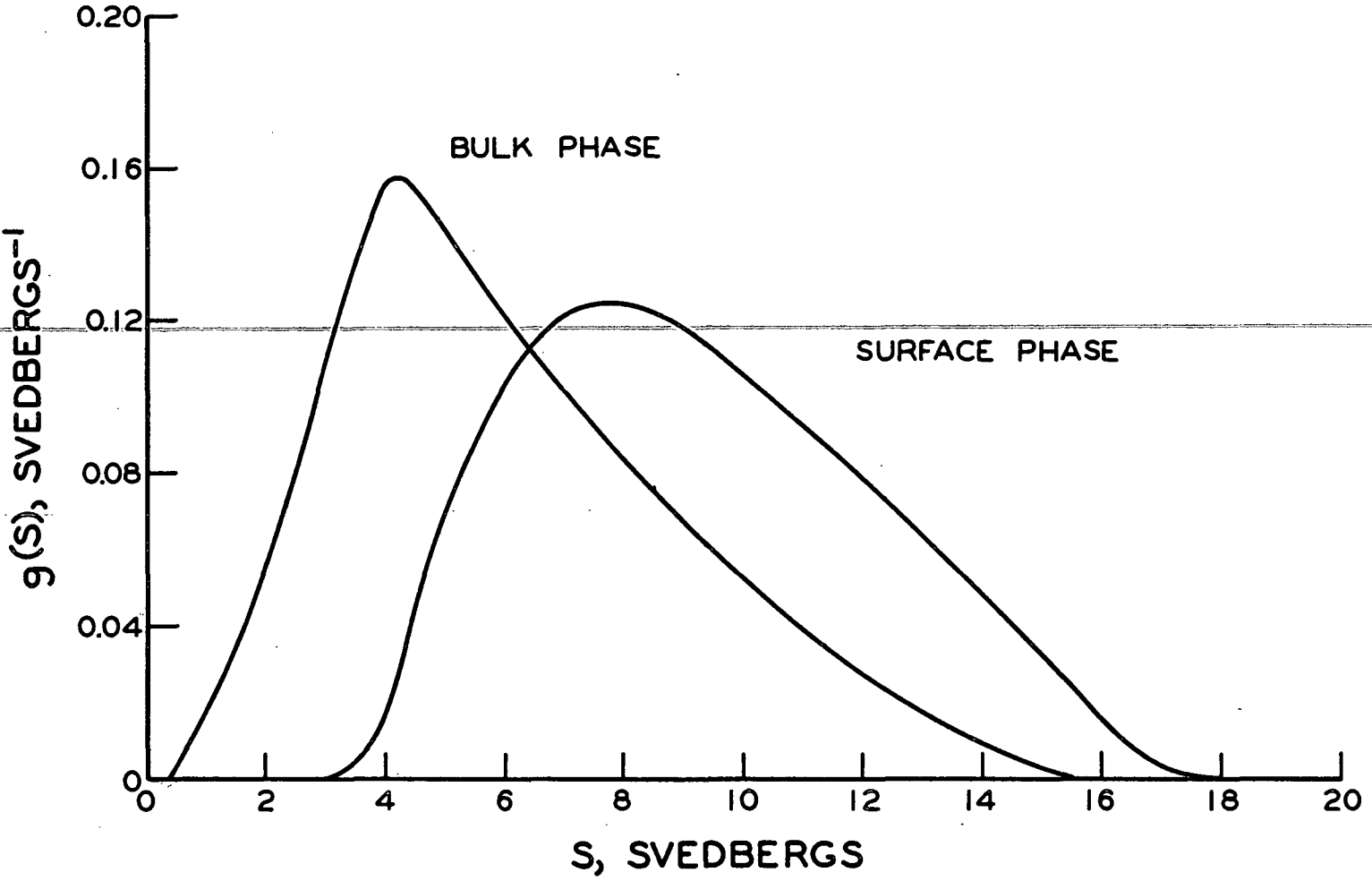

Figure 15. Normalized Distributions of Sedimentation Coefficients for Polystyrene PB6 Following Equilibrium Adsorption (Sample 6050)

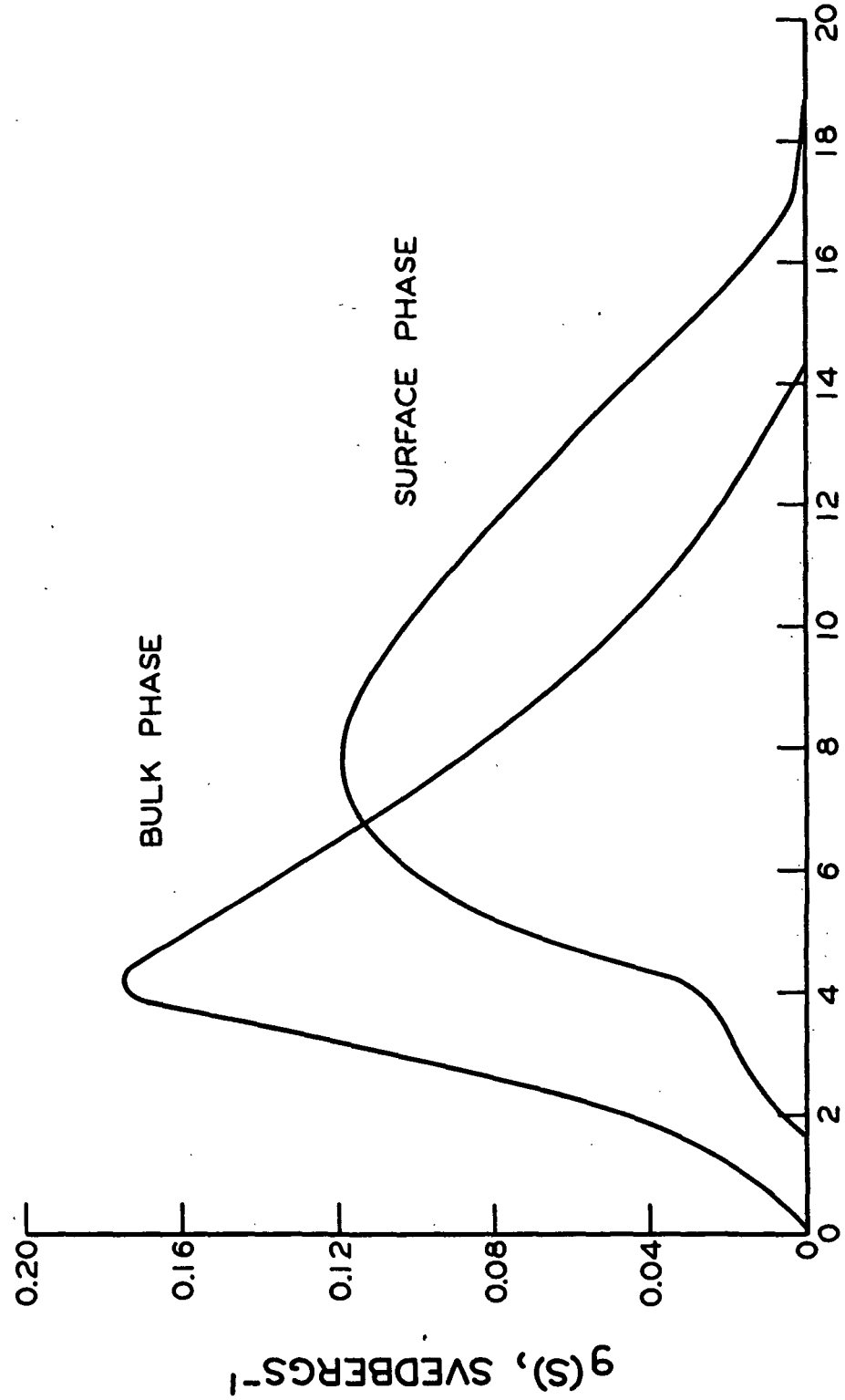

Figure 16. Normalized Distributions of Sedimentation Coefficients for Polystyrene PB6 Following Equilibrium Adsorption (Sample 6060)

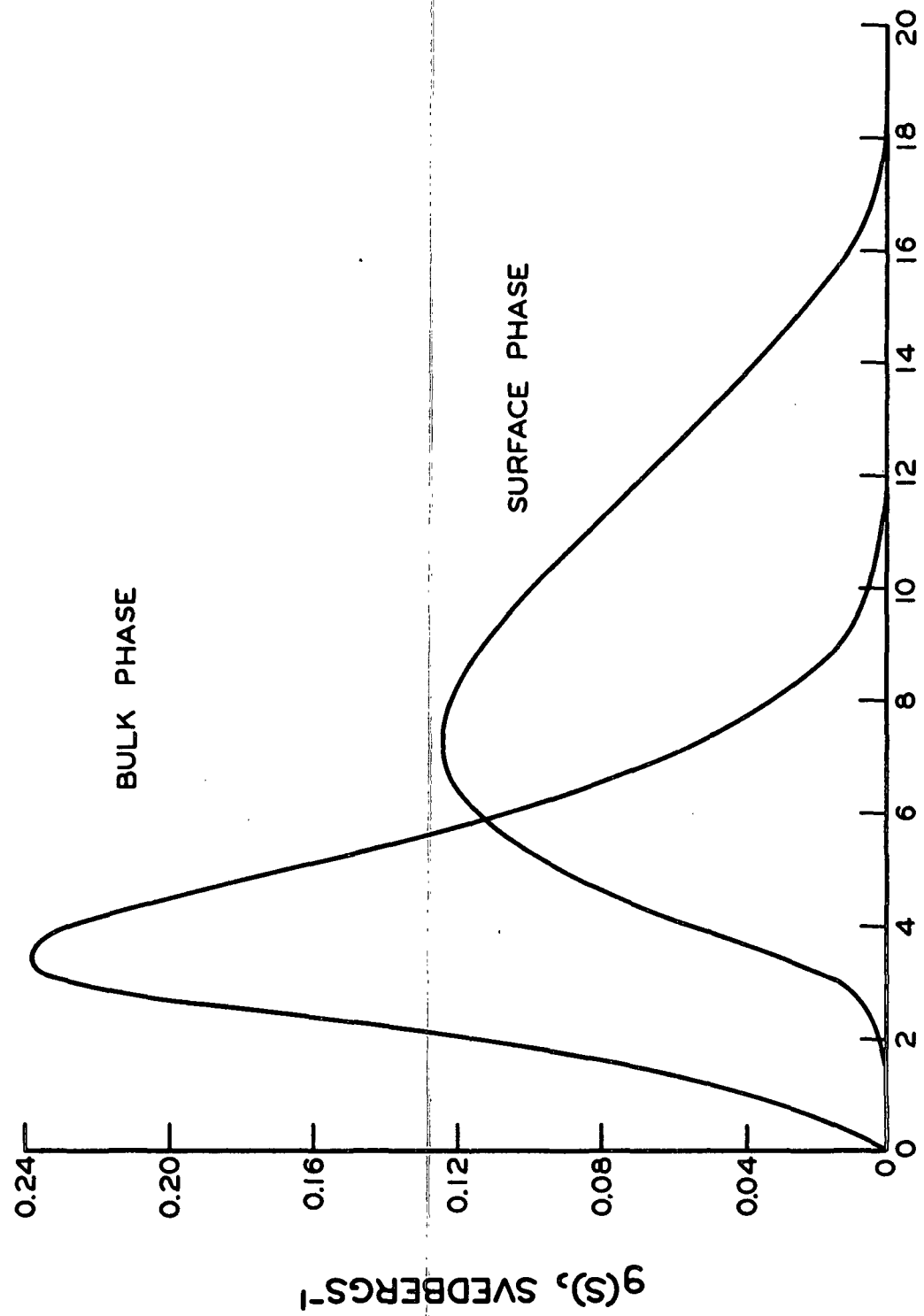

Figure 17. Normalized Distributions of Sedimentation Coefficients for Polystyrene PB6 Following Equilibrium Adsorption (Sample 6080)

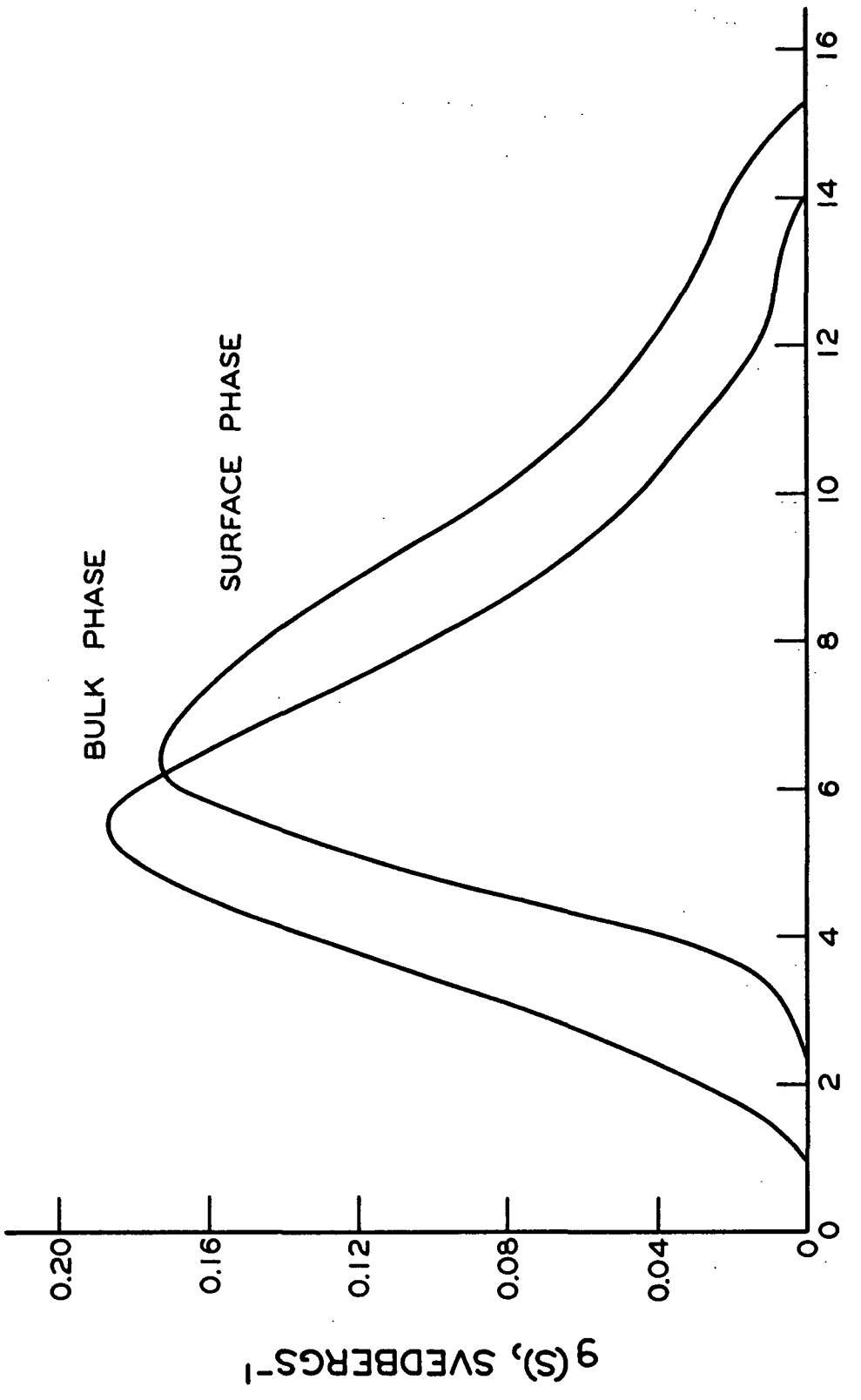

Figure 18. Normalized Distributions of Sedimentation Coefficients for Polystyrene PB5 Following Equilibrium Adsorption (Sample 5020)

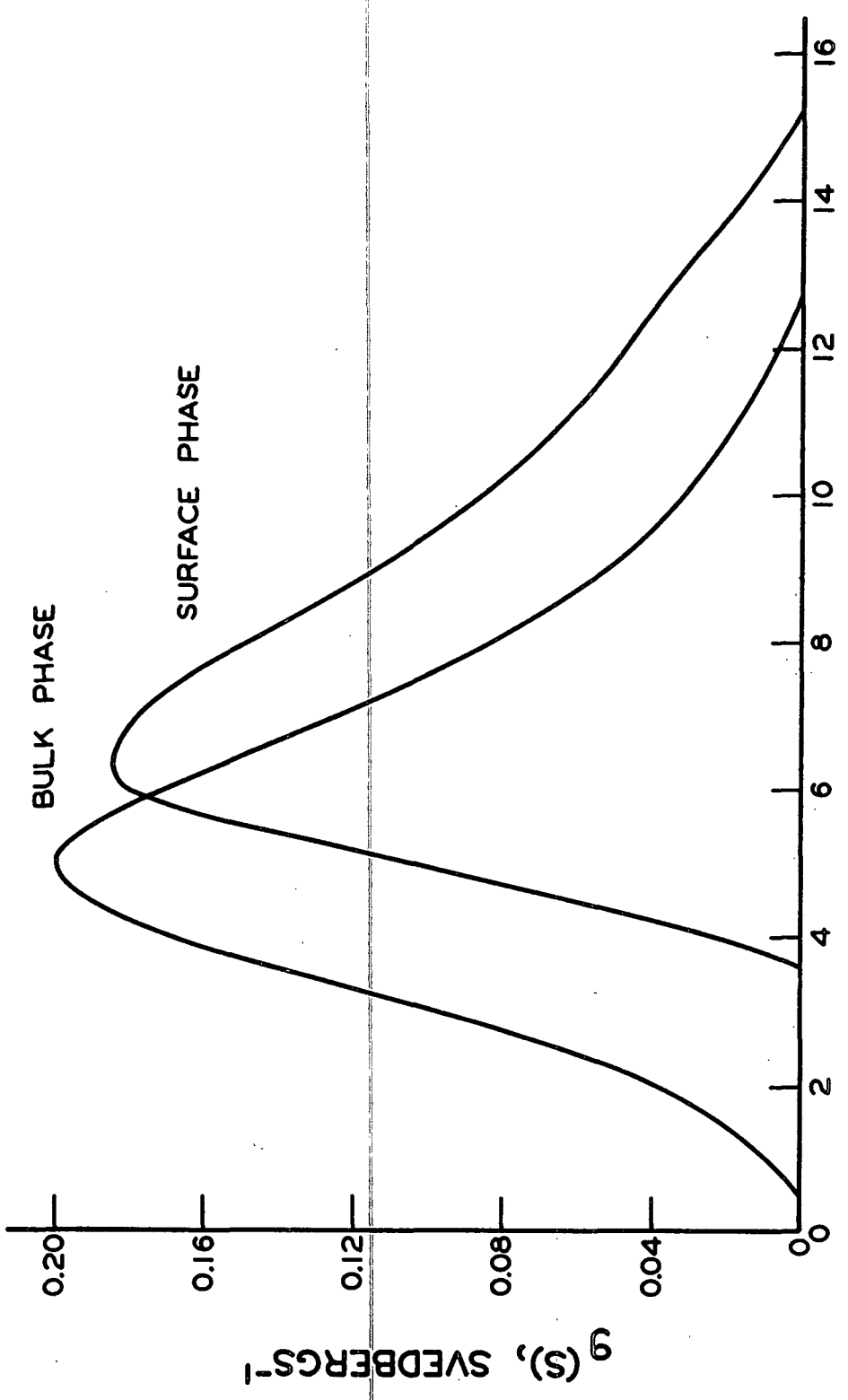

Figure 19. Normalized Distributions of Sedimentation Coefficients for Polystyrene PB5 Following Equilibrium Adsorption (Sample 5040)

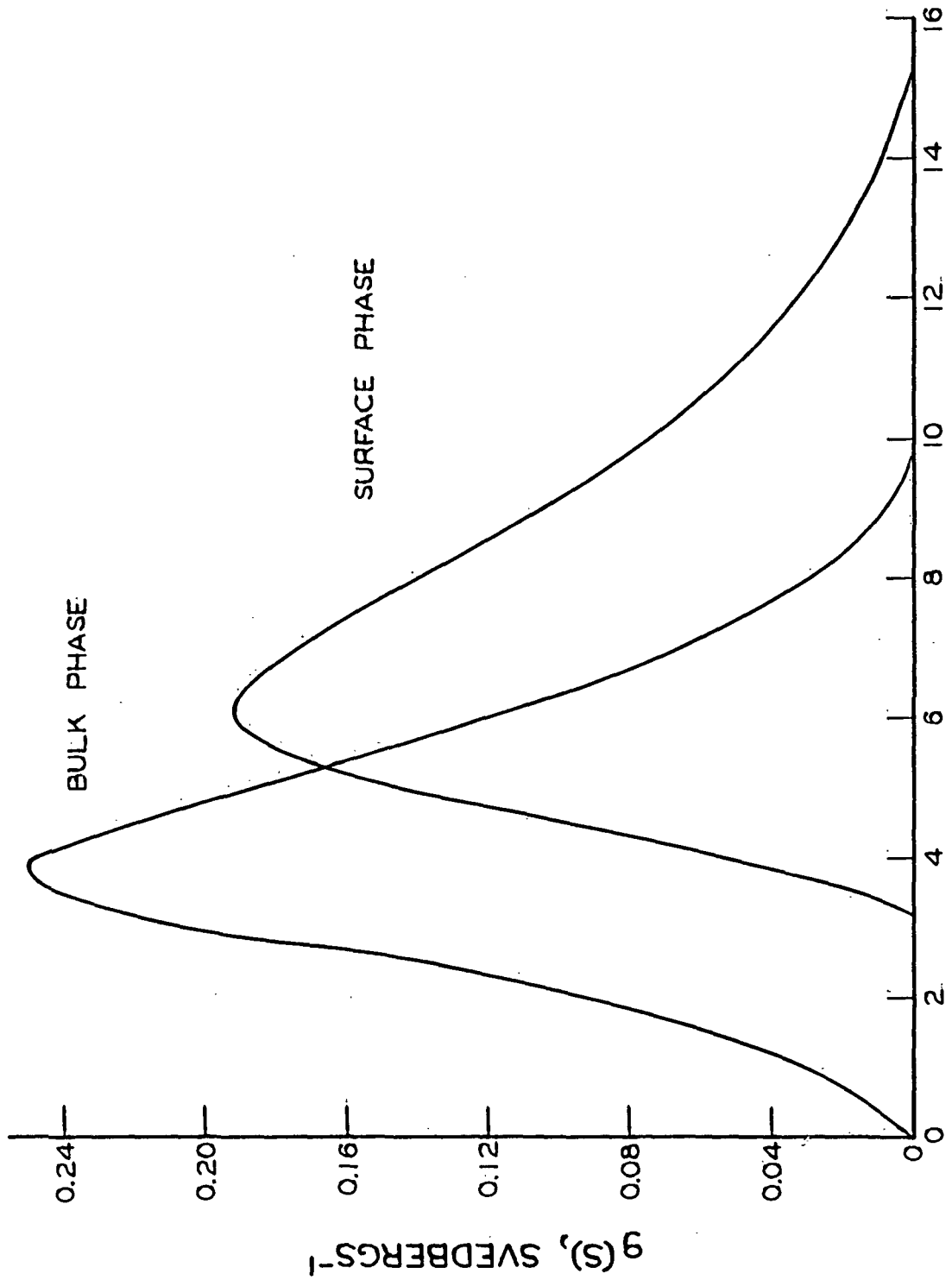

Figure 20. Normalized Distributions of Sedimentation Coefficients for Polystyrene PB5 Following Equilibrium Adsorption (Sample 5070)

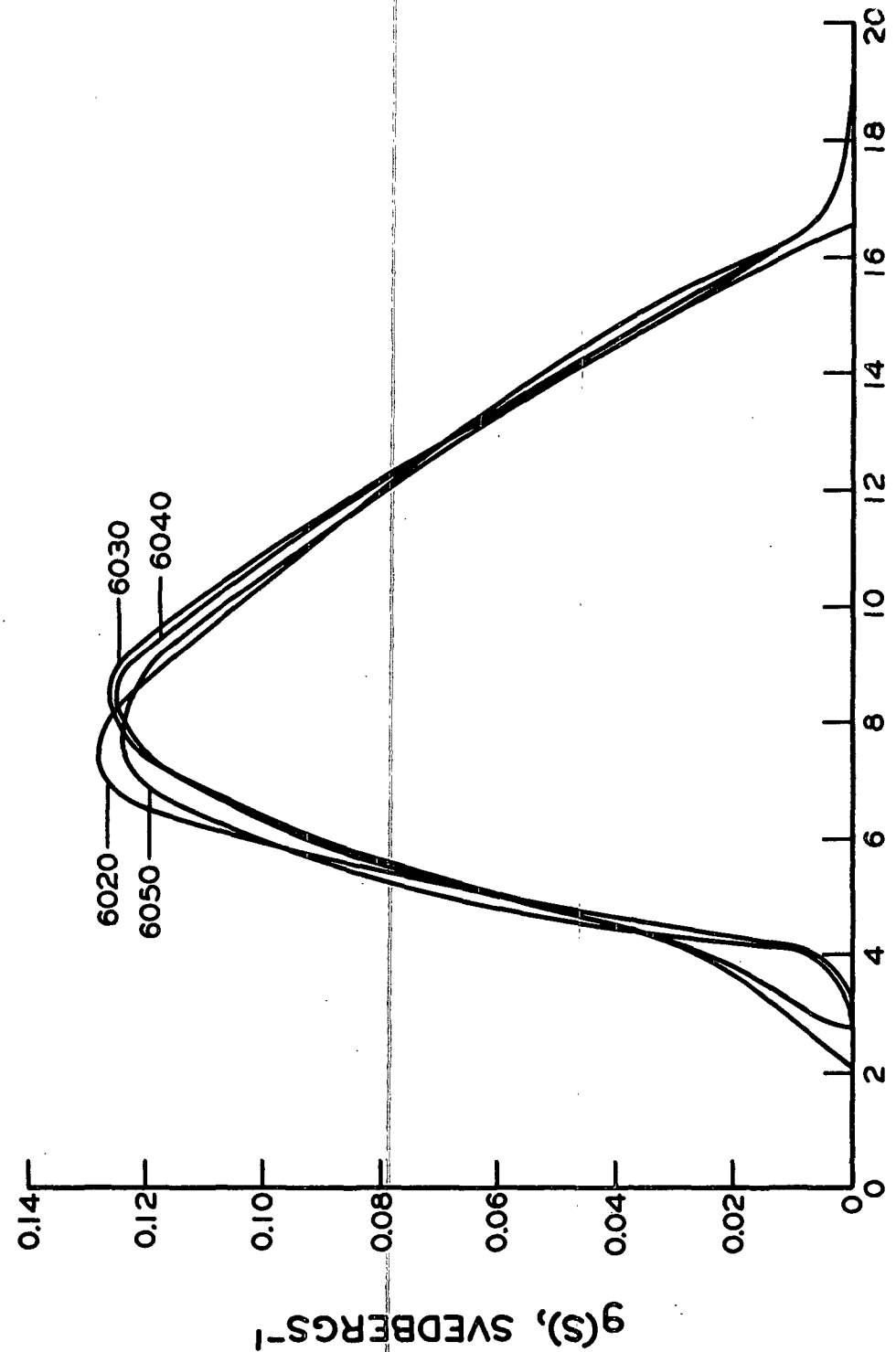

Figure 21. Comparison of Normalized Distributions of Sedimentation Coefficient for Surface Phase Samples 6020, 6030, 6040, and 6050

The distributions presented in Fig. 22 are taken from the bulk-phase distributions presented in Fig. 18-20 and the original distribution, Sample 5100, from Fig. 11. These distributions confirm the viscometric results presented in Fig. 6 that the higher molecular weight species are preferentially adsorbed. All of the bulk-phase distributions in Fig. 22 have less high molecular weight polymer present than the original distribution, which demonstrates the preferential adsorption of these species. Also demonstrated is that increasing values of $\underline{X}_A$ progressively decrease the amount of high molecular weight material present, which would result in a continual decrease of the bulk phase intrinsic viscosity with increasing values of $\underline{X}_A$ as shown in Fig. 6.

A problem with the ultracentrifuge data is presented in Fig. 22. At the trailing end of the distribution, low values of $\underline{S}$, the distribution curves do not intersect at a common point. The original distribution has a greater $\underline{S}$ value at $\underline{g}(\underline{S}) = 0$ than do the bulk phase samples, and, as the value of $\underline{X}_A$ is increased, the discrepancy of the $\underline{S}$ values from the original distribution, at $\underline{g}(\underline{S}) = 0$ becomes greater. This appears to indicate that there is low molecular weight polymer in the bulk-phase samples that was not present in the original distribution. This could be taken as evidence of polymer degradation. The rate data for long equilibration times, Table V, however, indicate that polymer degradation was not occurring, and all of the equilibration periods for the samples used in the ultracentrifuge analyses had equilibration times of 4 days. Further evidence against degradation is provided by the reversibility experiments which were found to have the same equilibrium intrinsic viscosity after contact times of 8 to 12 days depending on the experiment. In the reversibility work, the order of addition of the high and low molecular weight polymers was varied. Therefore, the adsorption contact times for each polymer were varied, but the systems were found to attain the same equilibrium condition independent of the time a particular

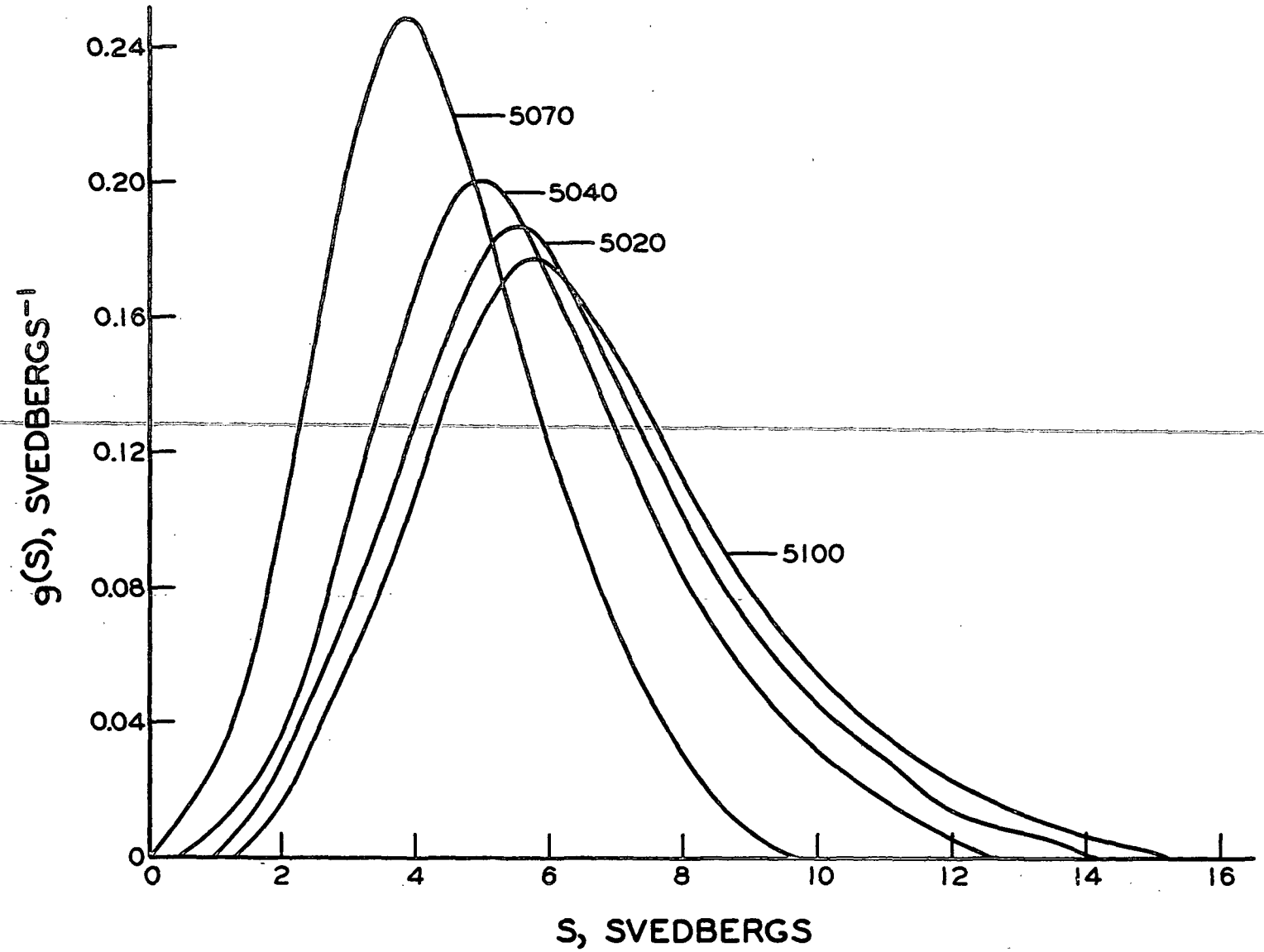

Figure 22. Comparison of Normalized Distributions of Sedimentation Coefficient for Bulk Phase Samples 5020, 5040, 5070, and Original Sample 5100

sample was in contact with the adsorbent. It is the author's opinion that the rate and reversibility experiments are good evidence that degradation of the polymer was not occurring. The study by Emery (22) led to the same conclusion.

The problem is thought to have an explanation in terms of the mutual enhancement of velocities of two particles sedimenting in an infinite media. Famularo and Happel (67) and Stimson and Jeffery (68) have discussed this enhancement from a theoretical basis. For two particles sedimenting as a vertical doublet, the velocity of the doublet will be greater than the velocity of either of the particles sedimenting alone. Kaye and Boardman (69) have experimentally demonstrated that a cluster of particles will sediment at a greater velocity than a single particle.

It seems reasonable to expect that the enhancement of the velocity of a small particle by a larger one would be greater than the enhancement of the velocity of the smaller particle by the presence of a particle of the same size. In the ultracentrifuge experiments, the polymers having low sedimentation coefficients displayed higher sedimentation values at low levels of $\underline{X}_A$, when most of the large polymers were present in the bulk phase. It is believed that the presence of the large polymers which have high sedimentation coefficients enhanced the sedimentation velocity of the small polymers which have low sedimentation coefficients. As these larger polymers were preferentially removed from the bulk phase, increasing values of $\underline{X}_A$, the enhancement of the sedimentation coefficient of the smaller polymers was reduced. Therefore, as the value of $\underline{X}_A$ was increased, a shift of the sedimentation coefficient of the smaller polymers to lower levels was observed. This is thought to be the explanation of the discrepancies observed on the trailing side of the distribution curves shown in Fig. 22. This explanation is consistent with the rate and reversibility experiments while that of polymer degradation is not.

Partitioning of Polymer Homologues Between the Surface and Bulk Phases

The reversibility experiments presented evidence for thermodynamic equilibrium, and from this it may be expected that a relationship between the distribution of polymer homologues in the surface and bulk phases can be determined. Emery (22) studied the partitioning and found that the relationship for the distribution of polymer homologues between phases may be expressed as follows:

$$\ln(N_x'/N_x) = B[\ln(x)] + \ln(D) \qquad (36)$$

where D and B are the intercept and slope, respectively, for the observed linear relationship, x is the degree of polymerization (D.P.), and N_x' and N_x are the number of species having D.P. = x in the surface and bulk phases, respectively.

The ratio, N_x'/N_x, was calculated by assuming that the molecular weight distribution, and, therefore, the sedimentation coefficient distribution, was continuous. This assumption is expressed as follows:

$$N_x'/N_x = X_A g_A(S)/X_B g_B(S) \qquad (37).$$

In an attempt to extend Emery's work (22), the surface and bulk phase data from the present work were calculated according to Equation (36). It was found that these data did not give a satisfactory fit to the equation determined by Emery.

Equation (1) (p. 9) can be rearranged to relate the partitioning of a polymer homologue to its D.P. as follows:

$$\ln(N_x'/N_x) = -\lambda x + \ln(A\delta/V) \qquad (38).$$

The bulk and surface-phase data were plotted according to this equation as $\ln(N_x'/N_x)$ versus x. These data are presented in Fig. 23 and 24 for Samples PB5 and PB6, respectively, at each level of X_A studied.

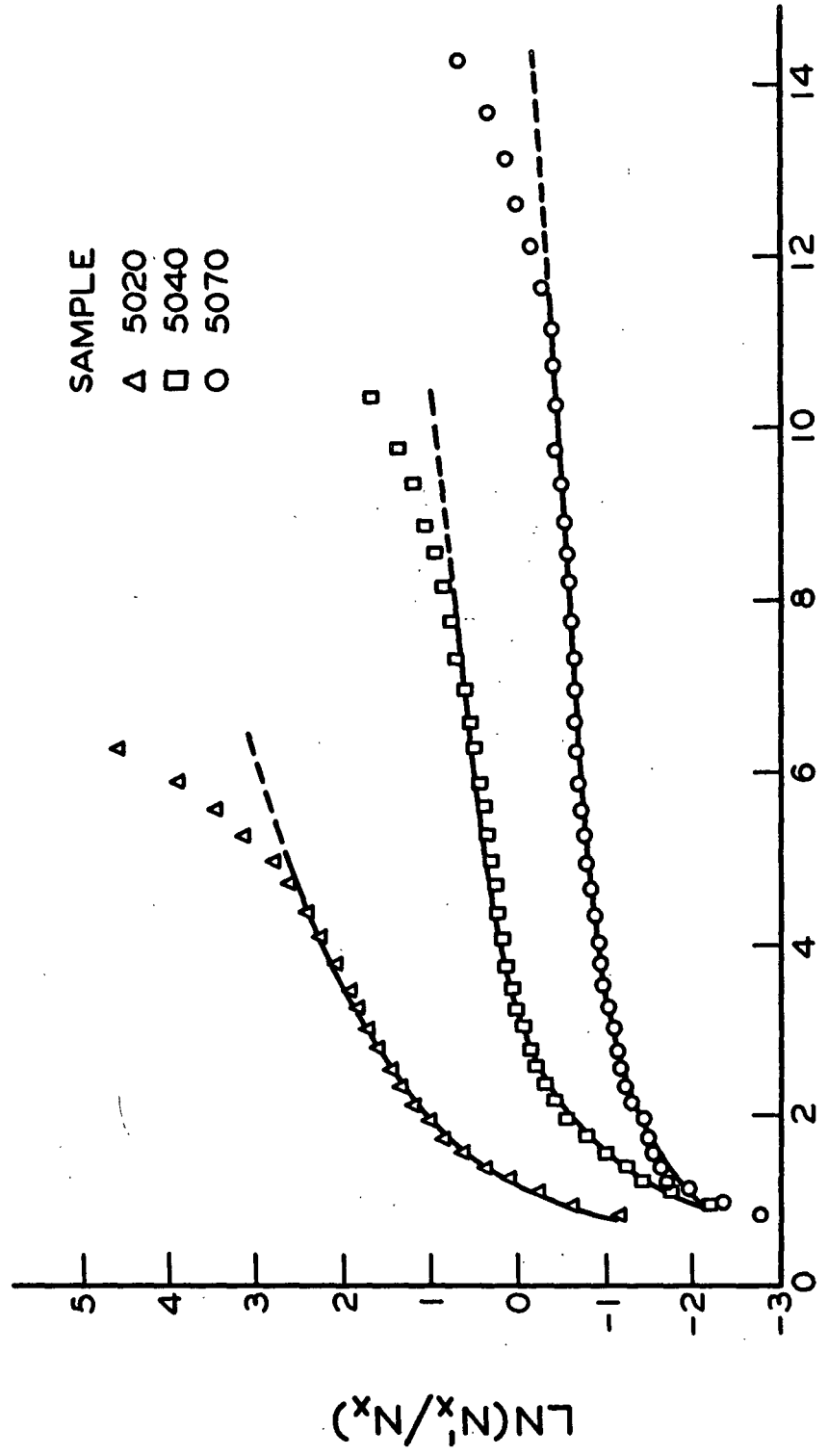

Figure 23. Partitioning of Polymer Homologues Between the Bulk and Surface Phases for Polystyrene PB5

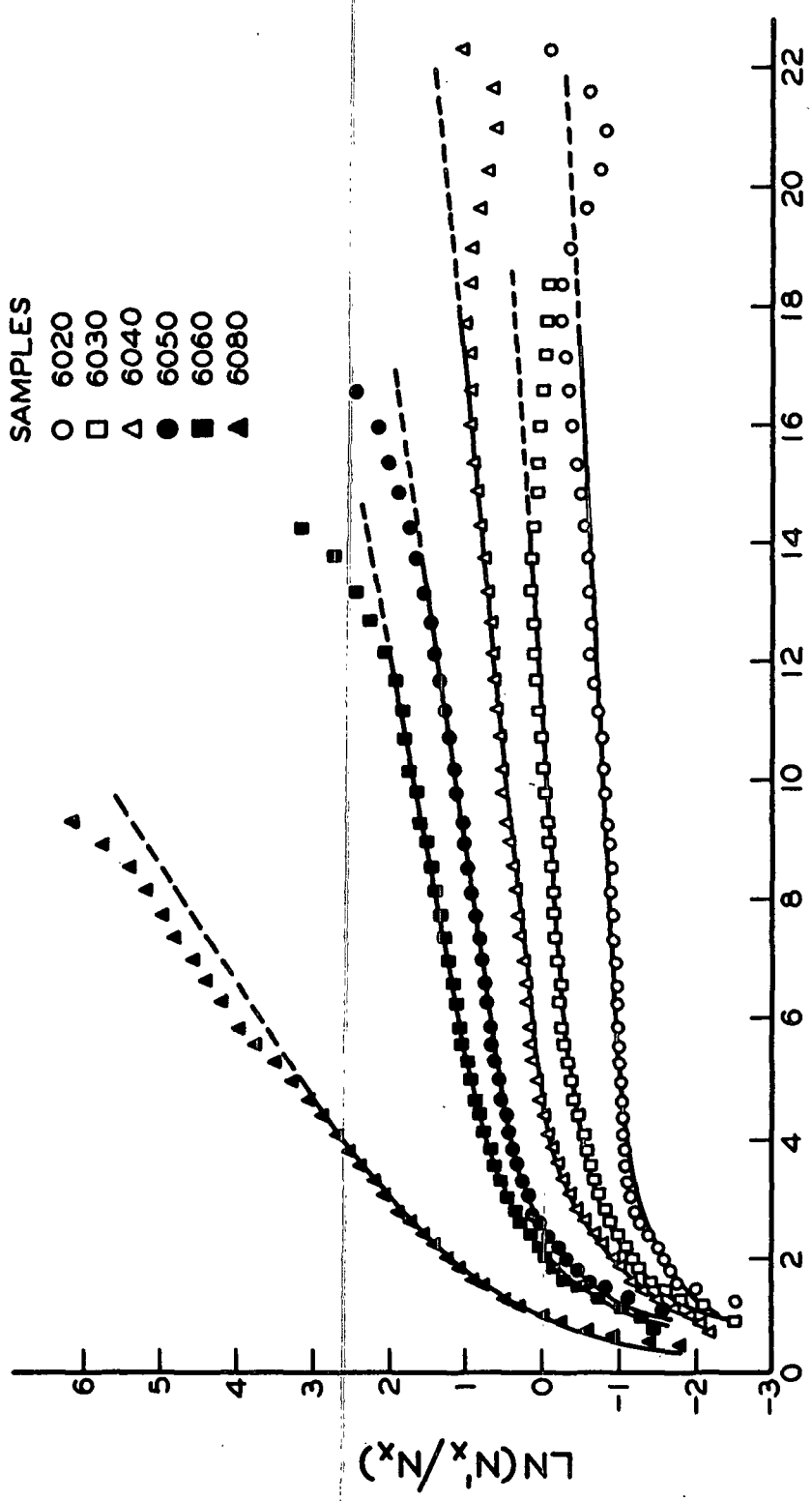

Figure 24. Partitioning of Polymer Homologues Between the Bulk and Surface Phases for Polystyrene PB6

Each data set, at a constant value of $\underline{X}_A$, may be fitted to an equation in the form:

$$\ln(N_x'/N_x) = F + H\,x + I\,[\exp(-x)] \qquad (39)$$

as shown by the solid curves through the data points. (Note: in the calculations, the $\underline{x}$ values were scaled by a factor of 1/1000.) The coefficients of the regression expressions for the partitioning data are summarized in Table XI.

TABLE XI

REGRESSION RESULTS FOR THE PARTITIONING RELATIONSHIP

Sample	$\underline{X}_A$	Partitioning Coefficients $\underline{F}$	$\underline{H}$	$\underline{I}$
6020	0.221	-1.267	0.052	-2.952
6030	0.327	-0.711	0.068	-4.262
6040	0.424	-0.326	0.082	-4.812
6050	0.523	-0.096	0.105	-4.624
6060	0.614	-0.266	0.142	-4.396
6080	0.820	0.670	0.509	-2.986
5020	0.238	-1.134	0.070	-2.894
5040	0.413	-0.139	0.110	-5.135
5070	0.709	1.052	0.329	-4.986

The relationships between the coefficients, $\underline{F}$, $\underline{H}$, and $\underline{I}$, and the experimental parameter, $\underline{X}_A$, were determined from plots of the appropriate quantities as shown in Fig. 25 and 26.

The coefficient, $\underline{I}$, was taken to be independent of $\underline{X}_A$ and assigned its average value, $\underline{E}$.

$$I = E \qquad (40).$$

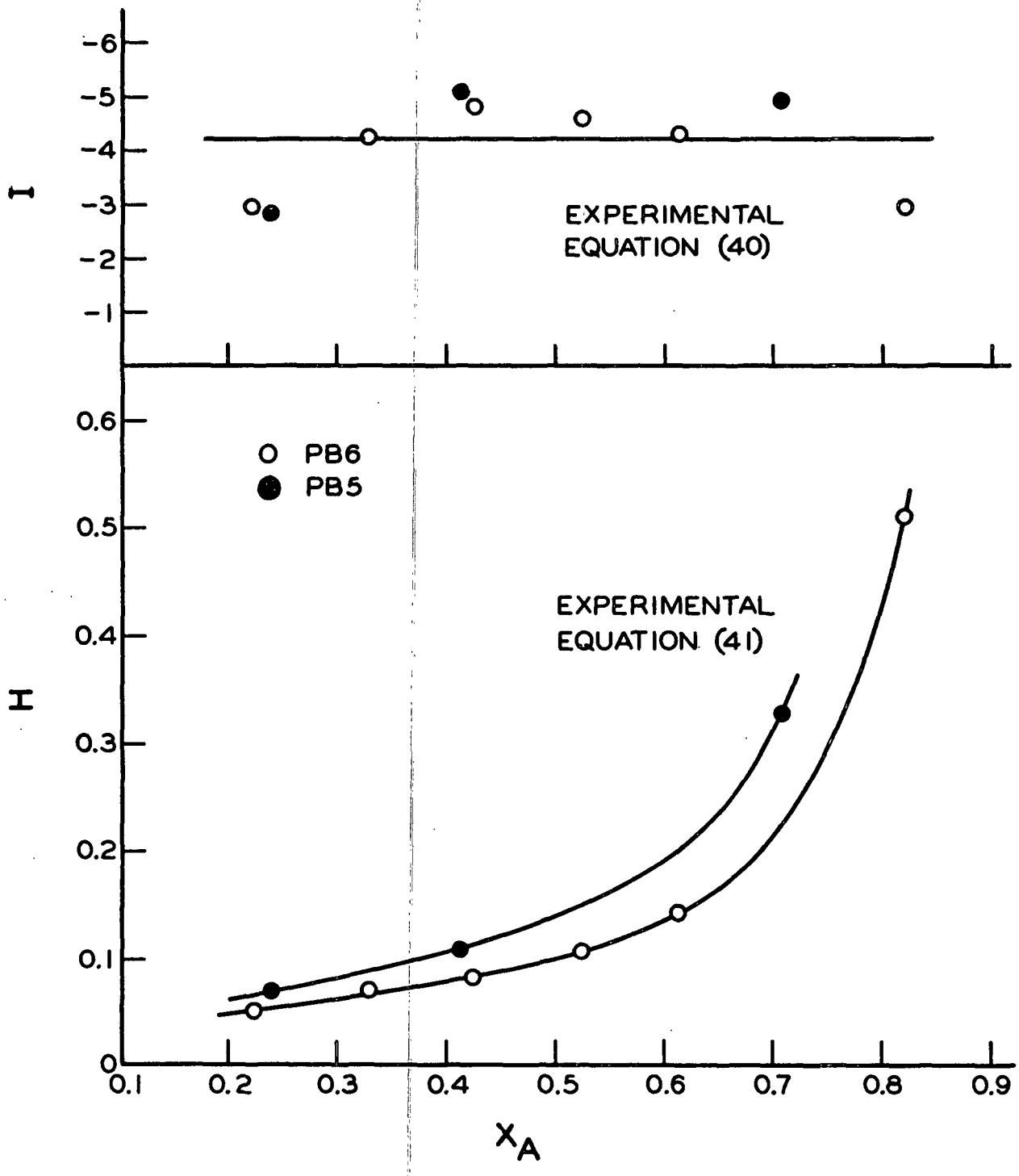

Figure 25. Coefficients H and I from Partitioning Equation (39)

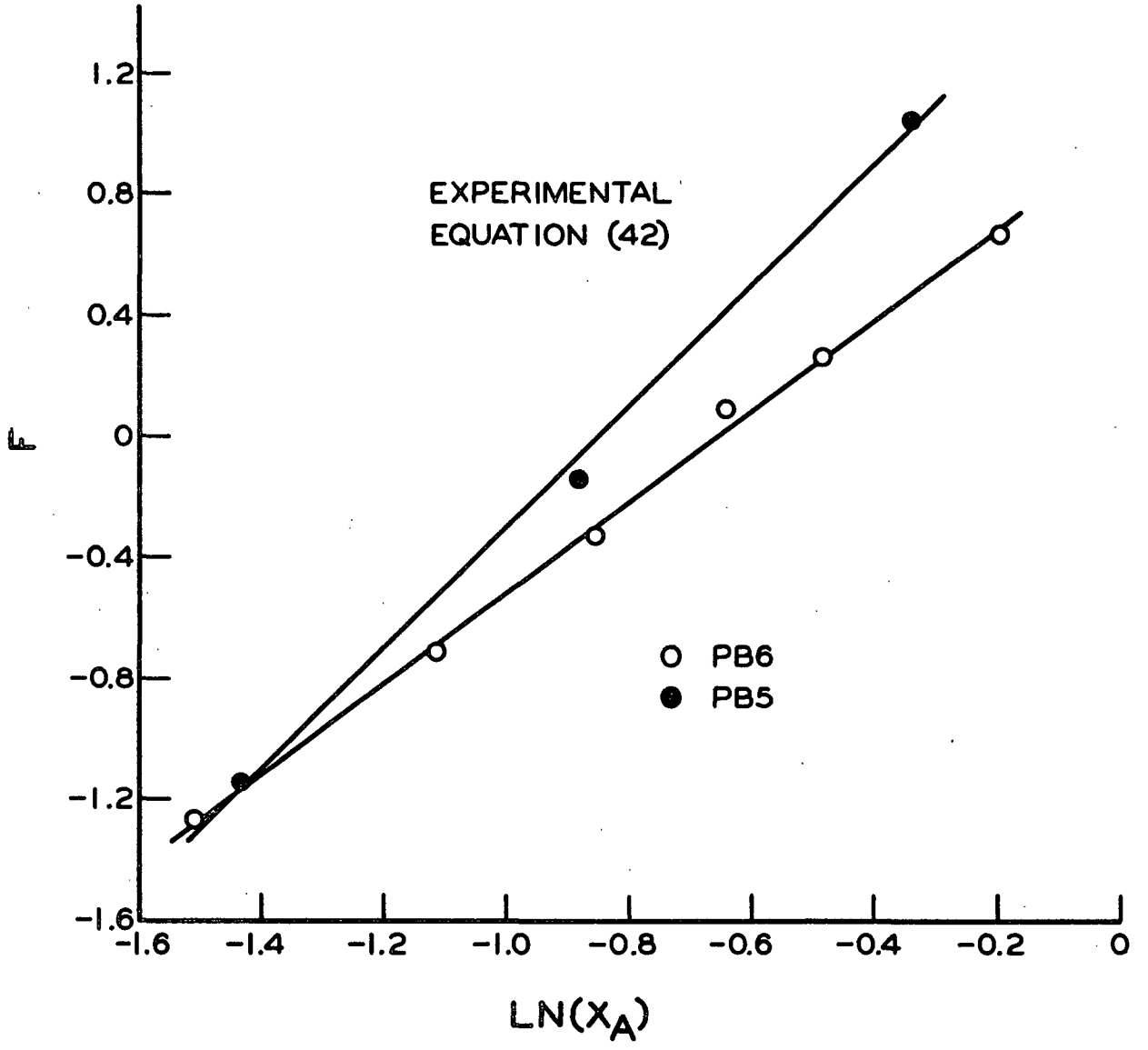

Figure 26. Coefficient F from Partitioning Equation (39)

The coefficient, H, was related to X_A by an equation of the form:

$$H = J + L(X_A) + P\,[\exp(QX_A)] \qquad (41)$$

where J, L, P, and Q are regression coefficients. It is interesting to note that the coefficient, H, was a linear function of X_A over the same range of X_A values for which the surface-phase distribution was found to be nearly independent of X_A (see Fig. 21). The coefficient, F, was related linearly to $\ln(X_A)$ as follows:

$$F = R + T\,[\ln(X_A)] \qquad (42)$$

where R and T are regression coefficients.

Equations (40), (41), and (42) may be combined with Equation (39) to obtain the following generalized partitioning relationship:

$$\ln(N_x'/N_x) = R + T\,[\ln(X_A)] + \left\{J + L(X_A) + P[\exp(QX_A)]\right\}_x + E[\exp(-x)] \qquad (43).$$

The values of the coefficients in Equation (43) for Samples PB5 and PB6 are presented in Table XII.

TABLE XII

NUMERICAL VALUES OF THE COEFFICIENTS IN THE GENERALIZED PARTITIONING EQUATION[a]

Name of Coefficient	Sample PB5	Sample PB6
R	1.705	0.996
T	2.004	1.503
J	0.0209	0.0199
L	0.204	0.142
P	4.360×10^{-5}	2.759×10^{-5}
Q	11.61	11.61
E	-4.150	-4.150

[a] Equation (43).

Figures 23 and 24 show that at high values of $\underline{x}$ there is some deviation of the data from the curves calculated with Equation (39). (For this discussion, a particular sample, PB5, $\underline{X}_A$ = 0.413 g./g., was selected for illustration, but the discussion is general and applies to the other samples as well.) This deviation results from the requirement of the partitioning expression that all of the species present in the original polymer before adsorption be present in the bulk phase and that only the amount of a polymer homologue can vary. It is seen from Fig. 19 that the distribution, as measured, has no polymer species with sedimentation coefficients greater than 12.75 svedbergs. The original distribution, PB5, contains species having $\underline{S}$ values extending to 15.0 svedbergs.

Since the partitioning expression requires that the bulk-phase distribution contain species with values of $\underline{S}$ greater than 12.75 svedbergs, the measured distribution understates the value of $\underline{g}_B(\underline{S})$ on the leading side of the boundary. From Equation (26) it can be seen that this also results in an overstatement of $\underline{g}_A(\underline{S})$ at equivalent values of $\underline{S}$. Therefore, the term, $\underline{N}_x'/\underline{N}_x$, related to the distribution through Equation (37), is greater than predicted by the partitioning distribution. The result is a deviation of the experimental partitioning data, Fig. 23, upward from the curve calculated from Equation (39). It is thought that this discrepancy is one of experimental nature rather than a change of adsorption behavior because the discrepancy of the data appears at the leading edge of the distribution rather than at a particular value of the molecular weight. In the tail regions, the ultracentrifuge data were the most difficult to obtain because the base line on the schlieren photos intersected the boundary in that area and convective disturbances in the solution were generally observed at the high molecular weight tail.

The difference between the calculated curves and the data in Fig. 23 and 24 is put in better perspective by calculating the distribution of S versus $g_B(S)$ from the generalized partitioning expression, Equation (43), at X_A = 0.413 g./g. and comparing this distribution with the distribution obtained experimentally. The two distribution curves are shown in Fig. 27. The agreement between the two distributions is excellent except at either tail. The discrepancy on the trailing tail, low values of S, will be discussed later. The difference between the two distributions on the leading tail, high values of S, is not large, and considering the replicate samples of the original PB6 distribution, Fig. 10, the difference could be attributed to experimental scatter. It is the author's opinion that the ultracentrifuge technique used in this study was not sensitive enough at the leading tail to precisely determine the small amounts of polymer present at high values of the sedimentation coefficient in the bulk-phase samples. This lack of precision is demonstrated in Fig. 24 by the partitioning curves for Samples 6020, 6030, and 6040, which deviate from the regression line at high values of x. This scatter indicates that the problem is of an experimental nature, rather than the result of a change in the adsorption behavior.

The deviation of the calculated distribution from the experimental distribution, Fig. 27, at the trailing side of the distribution, low values of S, results from the calculated distribution beginning at the same S value as the original distribution. The use of the original distribution is necessary to calculate the bulk-phase distributions. The variation of the intercept of the distributions along the S-axis with increasing values of X_A has been discussed previously.

Discussion of Theoretical and Experimental Partitioning Relationships

The experimental partitioning expression, Equation (43), is in good agreement with the theoretical expression, Equation (38), derived by Hoeve (7) with the

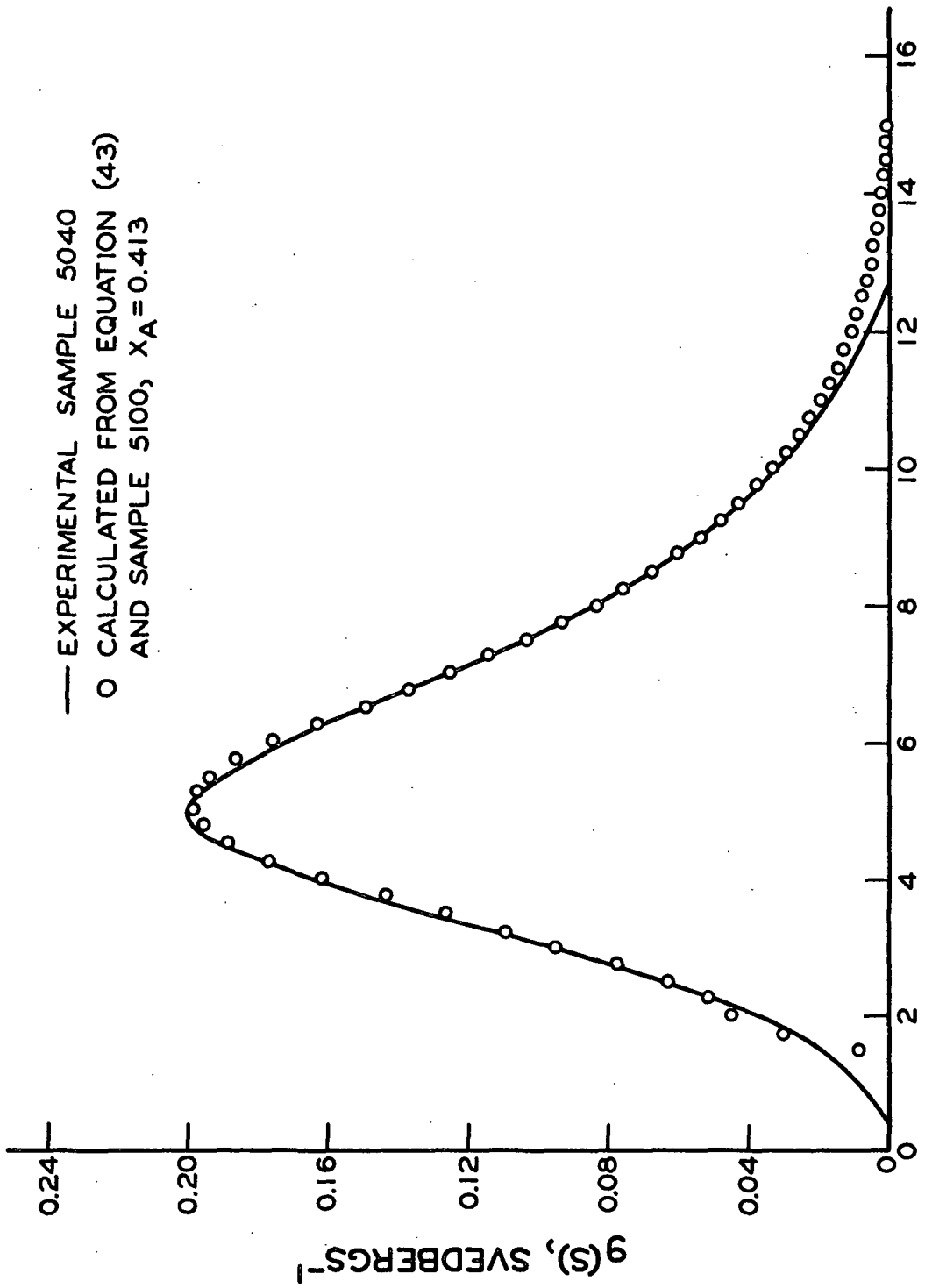

Figure 27. Comparison of Experimental Bulk-Phase Distribution with that Calculated from Generalized Partitioning Expression

exception of the term $\underline{I}$ [exp(-$\underline{x}$)]. There are two possible explanations for this additional term, neither of which are readily established as the only or even the predominant effect.

The theoretical partitioning expression was developed with the condition of monodisperse polymers of high enough molecular weight such that end-effects were not important. The experimental system employed a polydisperse polymer which contained high molecular weight species and also low molecular weight species. If end-effects change the adsorption behavior, then the tailing off of the partitioning curves, Fig. 23 and 24, at low values of $\underline{x}$ could result from end effects becoming important with the polydisperse polymer. It is difficult to speculate on this point since the effect of chain ends is not known. Nor is it known how high a molecular weight is necessary before the end-effect is not of importance to the partitioning expression developed by Hoeve. The end-effects could be appreciable with low molecular weight polymers; however, investigation of the effect is another study.

The other factor which could explain the deviation from the theoretical expression is the nonequal intercept of the distribution curves with the $\underline{S}$-axis on the trailing side of the distribution curves as discussed previously. Since the surface-phase distribution is calculated by difference, this distribution function will be understated at low values of $\underline{S}$ because the bulk phase is overstated or, perhaps more correctly, the original distribution function is understated. This is readily seen from Equation (26) which defines the calculation of the surface-phase distribution. An understatement of the surface-phase distribution leads to values of the term, $\underline{N}_{\underline{x}}'/\underline{N}_{\underline{x}}$, lower than expected and, therefore, a downward deviation of the partitioning data such as exhibited in Fig. 23 and 24.

If there is a change in the partitioning behavior with low molecular weight polymers, it is undoubtedly masked by the experimental problems with the ultracentrifuge, but neither effect can be corrected for in this study because the magnitude of the other effect is not known.

The effect of the term, $I\,[\exp(-x)]$, becomes small at values of x greater than approximately 3000 and above this value of x the experimental partitioning equation, Equation (43), has the same form as the theoretical equation, Equation (38). This indicates that the applicability of the theoretical equation is not limited by the restrictions of monodispersity or a theta solvent which were conditions of the derivation.

Conducting the experiments in a theta solvent would probably change the values of the parameters in the partitioning expression, for it is well established that the amount of polymer adsorbed is an inverse function of the solvating power of the solvent (14,20). That is, the amount of polymer adsorbed from a poor solvent is greater than the amount of polymer adsorbed from a good solvent. A change in solvating power apparently would not affect the partitioning expression, but it could affect the degree of partitioning at a particular molecular weight level.

The term $-\lambda$ in the theoretical partitioning expression was introduced in the description of the conformation of a polymer at the solid-liquid interface. This term, $-\lambda$, was taken to be equivalent to the parameter, H, from the similarity of Equations (38) and (39). As was previously noted, Fig. 25, the term, H, was nearly a linear function of X_A at low values of X_A. It may also be seen that the slope of the relationship is small. At low levels of X_A, it was found that the surface-phase distributions of species were nearly identical (Fig. 21). This indicates that in this range of X_A values the conformation of the adsorbed polymers

were equivalent; therefore, the term $\underline{H}$ is nearly constant. As the level of $\underline{X_A}$ was increased, the distribution of the polymers in the surface phase was altered, which resulted in a change of the average conformation of the polymers and an increase in the value of $\underline{H}$.

The values of the term, $\underline{H}$, for the two polymers studied, PB5 and PB6, were found to be different, but similar relationships to $\underline{X_A}$ were observed. Since the Polymer PB6 contained species having higher molecular weights than those in Polymer PB5, the difference in the levels of the term $\underline{H}$ was attributed to a different average conformation of the polymers in the surface phase. The term $\underline{F}$ in the experimental partitioning equation, Equation (39), was found to be a linear function of the quantity $\ln(\underline{X_A})$. From the defining equation of $\underline{X_A}$, Equation (20), it can be seen that this quantity contains the same relationship between the parameters $\underline{W_A}$ and $\underline{V}$ as are found in the theoretical partitioning equation, Equation (38), between the parameters $\underline{A}$ and $\underline{V}$. The parameter, $\underline{W_A}$, is directly proportional to $\underline{A}$.

Since the values of the parameters in the partitioning expression are dependent on the distribution of polymer species present, the absolute values of the parameters have limited value unless identical systems are studied. However, the experimental data confirm the form of the theoretical expression, and it would be expected that other polymer systems would have a partitioning expression similar to the theoretical one. Further work is necessary to determine how the parameters in the partitioning expression are dependent on the distribution of the adsorbing polymer.

Although the experimental partitioning expression in itself gives little evidence for thermodynamic equilibrium, the theoretical expression was derived on this basis and the experimental expression was found to have a similar form.

This information suggests thermodynamic equilibrium. The reversibility data presented in this study, together with previous experimental work in the literature, also present good evidence for the attainment of thermodynamic equilibrium in a polymer adsorption system. The system used in this study was limited to polymer-adsorbent interactions of the van der Waals' type, and other systems which result in larger interactions, such as hydrogen bonding, will require evidence of their own.

SUMMARY AND CONCLUSIONS

An investigation of the equilibrium behavior of a polymer adsorption system was made in this study. The system chosen had previously been studied by Emery (22) and consisted of polystyrene, carbon black, and 1,2-dichloroethane.

Solutions of polystyrene were mixed with the adsorbent for times long enough to establish equilibrium. The solution phase was separated from the solid phase and analyzed for intrinsic viscosity and concentration. Fractionation and reversibility behavior was adjudged from intrinsic viscosity measurements.

To determine molecular weight distributions of selected polystyrene samples, sedimentation velocity experiments were made on the ultracentrifuge. The data from these analyses were corrected for the effects of pressure, diffusion, and concentration.

The main experiments performed, their results, and conclusions drawn from the results are presented in the following summary:

Reversibility experiments were carried out with narrow molecular weight distribution polystyrene samples. These experiments were designed to determine whether the equilibrium condition of an adsorption system was dependent on the order of addition of the polymer samples when the final conditions of the experiment were maintained constant.

The results of the reversibility experiments demonstrated that the equilibrium condition of the system was independent of the order of addition of the polymer samples. This was studied in a two-polymer system where the order of addition and the concentration were varied and in a three-polymer system where the order of addition only was varied.

These experiments confirm the work by Emery (22) and Kolthoff and Gutmacher (9) that exchange of polymeric species occur between the bulk and surface phases. Since the equilibrium condition was found to be independent of the path to that condition, the results give good evidence of thermodynamic equilibrium.

Fractionation experiments were made with two broad molecular weight distribution polystyrene samples. The ratio of adsorbent to solution concentration was varied. It was found that the adsorption data could be expressed in terms of a Langmuir isotherm for the concentrations studied. The higher molecular weight sample was found to be adsorbed to a greater extent as qualitatively predicted by theoretical studies.

Intrinsic viscosity data from the bulk-phase samples were lower than those obtained for the original polymer and they were related by the weight fraction of polymer adsorbed. From the weight additivity of the viscometric quantities, the intrinsic viscosity values of the surface-phase samples were computed, and were found to be consistently higher than that of the original polymer. These results show that fractionation of the polymer occurred and the higher molecular weight species were preferentially adsorbed. The amount of fractionation was found to be dependent on the degree of polydispersity for the two distributions studied.

The sedimentation coefficient distributions, related to molecular weight distributions, were determined for selected adsorption experiments. The surface-phase distribution was calculated from the difference between the original and bulk-phase distributions. These distribution curves confirmed the intrinsic viscosity data which demonstrated that the higher molecular weight polymers were preferentially adsorbed. The sedimentation coefficient distributions for the surface phase at low levels of the weight fraction of polymer adsorbed show that

the surface-phase distribution established with an excess of adsorbable species was little affected by further excesses in concentration.

From knowledge of the sedimentation coefficient in the bulk and surface phases, the partitioning of a polymer homologue between the phases was calculated as a function of the degree of polymerization of that homologue. From these data a general partitioning expression was developed which contained parameters that were functions of the weight fraction of polymer adsorbed.

The experimental partitioning relationship was found to be in excellent agreement with a theoretical expression developed by Hoeve (7). The assumptions made in the theoretical treatment of a monodisperse polymer adsorbing from a theta solvent were not limiting as to the form of the relationship; however, the absolute quantities in the expression undoubtedly were. It was found that there were differences in the values of the parameters for the two broad distribution polymers analyzed, but the functional form of the relationship remained unchanged.

Since the theoretical relationship was developed on the basis of thermodynamic equilibrium and the experimental relationship was in good agreement, this is taken as evidence for thermodynamic equilibrium in the experimental system.

In conclusion, the reversibility experiments together with the partitioning expression provide evidence for thermodynamic equilibrium in this polymer adsorption system, this provides a good basis for the assumption of thermodynamic equilibrium made in the theoretical treatments of polymer adsorption.

GLOSSARY

A	total adsorbent area, $m.^2/g.$
B	regression coefficient
b	empirical constant
C_V	volumetric solution concentration, g./dl.
C_W	gravimetric solution concentration, %
D	regression coefficient
E	regression coefficient
F	regression coefficient
$f(M)$	differential weight distribution function of the molecular weight
$G(S)$	diffusion free differential weight distribution function, $svedbergs^{-1}$
$G^*(S)$	pressure corrected differential weight distribution function, $svedbergs^{-1}$
$G^*(S)_{max}$	maximum value of $G^*(S)$, $svedbergs^{-1}$
$g(S)$	corrected differential weight distribution function, $svedbergs^{-1}$
$g^*(S)$	apparent differential weight distribution function, $svedbergs^{-1}$
$g_A(S)$	surface-phase polymer, differential weight distribution function, $svedbergs^{-1}$
$g_B(S)$	bulk-phase polymer, differential weight distribution function, $svedbergs^{-1}$
$g_o(S)$	original polymer, differential weight distribution function, $svedbergs^{-1}$
H	regression coefficient
I	regression coefficient
J	regression coefficient
K	Langmuir equilibrium constant, cc./mg.
k	empirical constant
$k_{\alpha,\beta}$	intrinsic viscosity parameters
L	regression coefficient

M	molecular weight
N_f	number of polymers containing n segments in the bulk phase
N_p	number of polymers containing n segments in the surface phase
N_x	number of polymers of D.P. x in the bulk phase
N_x'	number of polymers of D.P. x in the surface phase
n	number of segments per polymer molecule
P	regression coefficient
Q	regression coefficient
R	regression coefficient
r	radius, cm.
r_i	radius ith specie, cm.
r_o	radius to original boundary, cm.$^{-1}$
S	sedimentation coefficient, svedbergs
S'	pressure corrected sedimentation coefficient, svedbergs
S^*	apparent sedimentation coefficient, svedbergs
$\overline{S^*_1}$	first moment of S^*, svedbergs
$\overline{S_1}$	first moment of S, svedbergs
$\overline{S_2}$	second moment of S, svedbergs
T	regression coefficient
t	time during ultracentrifuge run, sec.
t_e	equivalent time at maximum speed, sec.
t_o	solvent efflux time, sec.
t_s	solution efflux time, sec.
V	solution volume, cc.
x	degree of polymerization
Γ	specific adsorption, mg./g.
Γ_m	maximum specific adsorption, mg./g.

γ	k_α/k_β, intrinsic viscosity parameter
$\overline{\Delta n}$	refractive index increment
δ	a characteristic surface to adsorbed segment distance
η_r	relative viscosity
η_{sp}	specific viscosity
$[\eta]_A$	intrinsic viscosity of surface phase
$[\eta]_B$	intrinsic viscosity of bulk phase
$[\eta]_o$	intrinsic viscosity of original polymer
$\mathcal{K}$	pressure parameter
λ	Lagrangian multiplier, a measure of the conformation of an adsorbed polymer
μ	pressure parameter
ρ	solution density, g./ml.
ρ_o	solvent density, g./ml.
$\emptyset$	partial specific volume, ml./g.
ω	angular velocity, rad./sec.
ω_f	final angular velocity, rad./sec.

SUGGESTIONS FOR FUTURE RESEARCH

To the author's knowledge, the effect of the high molecular weight polymer on the velocity of the low molecular polymer in ultracentrifuge studies has not been reported previously. Valuable information with respect both to ultracentrifugation and hydrodynamics of sedimenting particles could be provided from a quantitative study of the effect. The use of narrow molecular weight distribution polymer samples would appear to be a logical choice for this investigation. The theoretical treatment and analysis of data would be very challenging but could also be very rewarding.

Further evidence for thermodynamic equilibrium in the polymer adsorption system could be provided by the demonstration of continuous exchange of polymeric homologues between the surface and bulk phases of the adsorption system at equilibrium. Knowledge of the partitioning behavior and the use of radioactively tagged narrow molecular weight distribution polymer samples appears to be necessary for such a study.

Emery (22) has suggested previously the use of a hydrogen-bonded system in a study similar to the present one. Since much of the polymer adsorption in the paper industry and also in biosynthesis apparently is via a mechanism of hydrogen bonding, such a study would be of widespread interest. A system similar to that employed by Fontana and Thomas (64) should be considered for the introductory phases to this study.

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